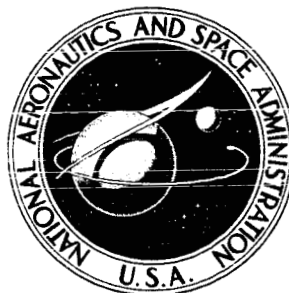


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REFERENCE

**CHEMICAL ANALYSIS
OF TUNGSTEN-URANIUM
DIOXIDE MATERIALS**

CLASSIFICATION CHANGED
To Unclassified
By authority of Len Oberg letter
Dated July 26, 1971
per msa

**Symposium
January 11-12, 1966**

*Lewis Research Center
Cleveland, Ohio*

Edited by William A. Gordon and William A. Dupraw

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1967

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ATOMIC ENERGY ACT OF 1954

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PREFACE

Cermets containing uranium dioxide particles dispersed in a continuous matrix of tungsten are relatively new nuclear materials with a wide range of applications in space nuclear propulsion and in power generation systems, as discussed in paper I.

To the analytical chemist, materials of this type do not fall into any neat category for purposes of chemical analysis. Although each of the constituent materials, tungsten and uranium dioxide, by itself presents some difficult problems to the analyst, new and difficult analytical problems are encountered when these materials are combined in the cermet. Experience by workers in the field has shown that analytical methods used routinely for either tungsten or uranium dioxide alone are not always suitable when these materials are combined in the cermet. For this reason, even laboratories with experience in the analysis of either of these constituents are likely to find considerable analytical development work necessary in order to analyze the cermet materials. With the introduction of oxide additives such as yttrium oxide, thorium oxide, cerium oxide, and gadolinium oxide into the cermet, the analytical problems are compounded. As a result of time required for analytical development work, the analytical services often lag behind the analytical needs of the related project, and the overall progress of the project may be adversely affected.

From associations of NASA - Lewis Research Center personnel with industrial contractors and other government agencies on work concerned with the tungsten water-moderated reactor program, it was clearly evident that a need existed for more complete exchange and documentation of information on methods of chemical analysis which had been developed in the various programs. For this reason, the NASA Lewis Research Center sponsored a symposium on chemical analysis of tungsten - uranium dioxide materials. Representatives from 15 industrial and governmental laboratories met on January 11 and 12, 1966, for the presentation of formal papers and informal discussion on the subject. A list of attendees is given at the back of this report.

The technical program included nine papers on analytical procedures and applicable laboratory techniques. These procedures and techniques cover the determinations of major metal constituents, trace metals, total oxygen, halogens, and special techniques for the determination of fuel stoichiometry. In addition to the formal presentations, a portion of the second day was devoted to a round-table discussion of problems of mutual interest and to amplification of the information presented formally. These proceedings include all the formal presentations and also a condensation of the discussion period.

A cross-referenced index of the methods presented, as well as other pertinent information, is given on page iv. The application of these methods to compositions other than those listed in the index for each particular method, may require additional development work to validate the method. This index, therefore, provides the essential details which will assist the analyst in judging if additional work is indicated for the compositions of interest to him. Those methods relating specifically to the determination of fuel stoichiometry provide only indirect measurements because they are predicated on certain assumptions about the physical nature of the solid state. The interpretation of the analytical data, therefore, can best be done by the materials researcher that requested the analysis. The reference index breaks this information down into summary form to facilitate this interpretation.

It is intended that the information reported in these proceedings, reflecting the broad experience of many laboratories, will not only prove helpful to chemists faced with the problem of analyzing tungsten - uranium dioxide materials but also will serve to inform the materials researcher of analytical capabilities which are not common knowledge.

William A. Gordon
Symposium Chairman

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|-------|---|--|---|---------------------|
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| III | U ⁰ ; Th ⁰ ; Y ⁰ | UO ₂ ; W-UO ₂ UO ₂ -ThO ₂ UO ₂ -Y ₂ O ₃ | Presence of free metal is used as a measure of substoichiometric O/U ratios. Not applicable to Mo-UO ₂ . | 132 |
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| V | Atomic emission | W-UO ₂ ; W-UO ₂ -Y ₂ O ₃ | Broad and sensitive elemental coverage are provided in a single analytical method. Additional work is indicated for routine analyses. | --- |

| VI | CO ₂ (from reduction of oxides by inductively heating sample in a graphite crucible) | U ₃ O ₈ ; W-UO ₂ ; UO ₂ -ThO ₂ ; UO ₂ -ZrO ₂ ; UO ₂ -SmO ₂ ; UO ₂ -Eu ₂ O ₃ ; UO ₂ -Gd ₂ O ₃ ; UO ₂ -Al ₂ O ₃ | Quantitative recoveries for oxygen are reported with relative standard deviations ranging from 0.2 to 1 percent. | 135, 136 |
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| VII | (1) Cl (2) F (3) N (4) W (5) U (6) Continuity of coatings (7) Ce (8) Rare earths (9) Y | (1) W, Ma, UO ₂ , W-UO ₂ (2) W, Ma, UO ₂ , W-UO ₂ (3) W, Ma, UO ₂ , W-UO ₂ (4) W-UO ₂ (5) UO ₂ , UO ₂ -ZrO ₂ , W-UO ₂ (6) W coated UO ₂ spheres (7) UO ₂ -CeO ₂ , W-UO ₂ -CeO ₂ (8) UO ₂ -rare earth (excl. Ce) (9) W-UO ₂ -Y ₂ O ₃ | These methods have been used extensively by NUMEC for analytical control in the production of nuclear materials. (8) Probably applicable to W-UO ₂ by initial separation of W using method for W in W-UO ₂ | --- |
| VIII | (1) Lattice spacing of UO ₂ (2) U ⁺⁶ ; U ⁺⁴ (3) O/U ratios (4) Free metal precipitates (5) C; F; W (6) U | (1) UO ₂ (2) UO ₂ (3) UO ₂ (4) W-UO ₂ (5) UO ₂ (6) W | (1) Estimation of O/U ratios (2) U ⁺⁶ is indicative of hyperstoichiometry (3) Oxidation-gravimetry (4) Microscopic examination of metallographic specimens (5) A microfluorine method is reported for small samples (6) ----- | --- 136 (fluorine) |
| IX | W; U | (1) U-W alloys; W-UO ₂ | ----- | |

^aThe compositions listed are those to which the method was applied as reported by the author in these proceedings. The applicability of the methods, however, is not necessarily restricted to these compositions.

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I. APPLICATIONS OF TUNGSTEN - URANIUM DIOXIDE

COMPOSITES IN SPACE NUCLEAR SYSTEMS

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National Aeronautics and Space Administration

Lewis Research Center

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SUMMARY

Tungsten - uranium dioxide composites are being considered for use in several high-temperature reactors proposed for use in space. The general features of several of these space propulsion and power generation systems are reviewed in this paper. In addition, some materials problems associated with the use of tungsten - uranium dioxide composites at high temperatures are presented to help define the areas requiring extensive use of chemical analyses.

INTRODUCTION

Several advanced nuclear systems being considered for either propulsion or electric power generation in space involve the use of tungsten - uranium dioxide fuel elements. These fuel elements consist of uranium dioxide particles dispersed in a continuous matrix of tungsten. This combination of materials satisfies the one common requirement of the different reactor systems - the need for a high-temperature (1200° to 2500° C) heat source. These high operating temperatures appear to be attainable with W- UO_2 composites because tungsten is compatible with UO_2 and both have high melting points (W, 3410° C; and UO_2 , $\sim 2800^{\circ}$ C).

As an introduction to this symposium on chemical analytical techniques used for these materials, this paper presents background information on some possible applications of W- UO_2 fuel elements and on the analytical data needed by researchers working with these materials. First, some of the nuclear systems which involve the use of W- UO_2 composites are described along with the associated operating requirements for W- UO_2 fuel elements. This description is followed by a discussion of the purity and

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stoichiometry requirements for the fuel currently used by the Lewis Research Center. Although these requirements specifically refer to fuel for a reactor system being investigated at Lewis, the reasons for the requirements are generally applicable to most high-temperature reactor systems with W- UO_2 fuel elements.

NUCLEAR SYSTEMS UTILIZING W- UO_2 FUEL ELEMENTS

Space Propulsion

Because nuclear rockets offer a considerable reduction in spacecraft weight for manned interplanetary missions as compared with current chemical rockets, a large research effort at several laboratories is directed toward development of nuclear rocket engines. This type of rocket utilizes fission-generated heat to expand hydrogen propellant gas, which subsequently is exhausted through a rocket nozzle to produce thrust. A schematic diagram of a typical reactor of this type is shown in figure I-1. As shown by the arrows in this illustration, liquid hydrogen is pumped through the nozzle walls and reflector to cool these parts. The gasified hydrogen is then directed through passages in the reactor core, where it is heated and expanded prior to exhausting through the nozzle.

This country's major nuclear rocket program (the KIWI-NERVA-PHOEBUS series of reactors) employs graphite-base fuel elements, but concurrently two alternate reactor concepts which utilize W- UO_2 fuel elements are under study. One of these is a fast reactor concept being examined at the Argonne National Laboratory (ref. 1), and the other is a thermal reactor concept being investigated at the NASA Lewis Research Center (ref. 2). Although there are basic differences in these reactor concepts, both of the systems would use tungsten-clad, W- UO_2 fuel elements that must operate in rapidly flowing hydrogen at temperatures up to about 2500°C . To allow for adequate preflight ground testing and in-flight maneuvering, these fuel elements must be capable of operating at the maximum temperature for up to 10 hours total operating time with at least 25 intermittent thermal cycles to the ambient temperature.

The primary materials difference in the fuel elements of these two concepts involves the amount of UO_2 dispersed in the tungsten. The fast reactor concept requires fuel loadings of the order of 50 to 60 volume percent UO_2 , while the thermal reactor concept would utilize loadings in the range of 10 to 30 volume percent. (This difference in fuel loading requires that analytical techniques used for these systems must be applicable to a wide range of compositions.)

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Space Power Generation

As more extensive spaceflights are undertaken in the coming years, the amount of electric power needed for this purpose will rapidly grow. For example, the unmanned Explorer XII satellite of a few years ago required only about 20 watts of power, the three-man Apollo mission to the moon will require about 2 kilowatts of power, and future manned trips to Mars may require 10 to 30 megawatts of power for electric propulsion. For the larger amounts of power, nuclear power generation systems appear quite attractive. Therefore, several methods of converting fission-generated heat to electric power are being investigated by various organizations. The two most promising nuclear power conversion systems are turbogenerator converters (both Rankine cycle systems and Brayton cycle systems) and thermionic converters.

The nuclear Rankine cycle and Brayton cycle turbogenerator systems are similar in that both would use a reactor to heat a fluid which would drive a turbogenerator system to produce electric power. The main difference in these systems is the working fluid; the Rankine cycle uses a two-phase liquid-vapor fluid, while the Brayton cycle uses a single-phase gas. Boiling and condensing liquid metals (Na, K, Li, etc.) would be employed in Rankine cycle space systems, whereas in Brayton cycle systems inert gases (Ne, Ar, Kr, etc.) would probably be used.

A schematic illustration of a turbogenerator system is shown in figure I-2. The two-loop system shown in this figure is the type most likely to be used in future space missions because it removes the reactor from the main working system and thereby reduces radiation shielding requirements. In this type of system, the heat generated in the reactor is carried by a liquid-metal fluid to the heat exchanger, where it is transferred to the working fluid of the power generation cycle. The heated working fluid is expanded through the turbine to drive the electrical generator. The fluid is further cooled in the radiator and compressed before completing the cycle. In the Rankine cycle, the liquid-metal working fluid is boiled in the heat exchanger and condensed in the radiator, while the working fluid in the Brayton cycle remains in a gaseous state throughout the cycle. The Rankine cycle is a more efficient system; however, lack of corrosion problems with inert gases and extensive experience with gas-driven turbomachinery suggest that a Brayton cycle may be more easily developed.

Several reactors currently are being developed for use in these turbogenerator, power generation systems. One of these involves the use of W- UO_2 fuel elements; this is the 710 Reactor being developed at the Nuclear Materials and Propulsion Operation of General Electric (ref. 3). The fuel elements in this fast reactor consist of tungsten-alloy-clad dispersions of UO_2 in W, with fuel loadings in the range of about 40 to 60 volume percent. The proposed operating temperature for these fuel elements is in the

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range of 1200° to 1600° C. Although this operating temperature is considerably lower than that of nuclear rocket fuel elements, the materials problem can be just as severe, since space power generation systems must operate unattended for extremely long durations (greater than 10 000 hr).

The other nuclear method for electric power generation involves thermionic converters in which fission generated heat is converted to electricity through the thermionic emission of electrons. The principal components of these converters (or diodes) are a high-temperature, electron-emitting surface (the cathode) and a lower-temperature, electron-collecting surface (the anode) separated by a gap containing cesium vapor to prevent buildup of space charge. In such a system, the voltage generated across the electrodes can be used to meet spacecraft power requirements.

The chief advantage of thermionic converters is their lack of need for rotating turbo-machinery, which should improve system reliability. However, this advantage is partly counterbalanced by the fact that numerous diodes (several hundreds) must be connected in series to achieve a sufficient power level since each diode generates only a small amount of power (~ 10 W/cm² of emitting surface). This requirement for high reliability in a large number of components is quite stringent.

A schematic diagram of a thermionic-reactor power system is shown in figure I-3. This diagram shows a network of cylindrical thermionic diodes which are stacked inside tubes. The central region of each converter is filled with the nuclear fuel which is clad with a material that serves as the emitting surface of the diode. Surrounding this emitter is a cylindrical collector which is separated from the emitter surface by a thin gap (0.005 to 0.015 in.). The collector is attached to the containment tube by use of an electrically insulating material, and the entire assembly is maintained at the desired temperature through use of a liquid-metal coolant that flows around the outside of the diode containment tubes. As shown in figure I-3, this coolant is continually pumped through the core in a recirculating system.

Since fuel temperatures of the order of 1500° to 1800° C are desired in thermionic converters, W-UO₂ composites also are being considered for use in this type of system. These composites would utilize fuel loadings in the range of 50 to 80 volume percent UO₂. Fueled diode development studies currently are being conducted by several organizations including the Division of General Dynamics (ref. 4) and the Special Purpose Nuclear Systems Operation of General Electric (ref. 5).

Since thermionic systems must also be able to operate continuously for 10 000 hours or more, two very stringent requirements on the fueled diode are

- (1) The emitter surface must not become contaminated with foreign materials since this could alter its work function.
- (2) The emitter must not change dimensionally since this would change the closely controlled spacing between the emitting and collecting surfaces.

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Both of these changes could decrease the efficiency of the converters. Therefore, close control of the materials must be maintained in initial preparation, processing, testing, and eventual operation.

CHEMICAL REQUIREMENTS FOR W- UO_2 COMPOSITES

Purity of Materials

An important requirement for the W- UO_2 fuel elements used in space nuclear systems is that of high purity. This is necessary because the extremely high operating temperatures for these reactors require that elements or compounds which (1) have melting points below the reactor operating temperature, (2) have high vapor pressures at these temperatures, or (3) will react with tungsten or UO_2 must be restricted to low concentrations. Experimental results have indicated that even small amounts of some impurities can cause a decrease in the operating capability of W- UO_2 fuel elements.

Although the effects of individual impurities are not fully known, reasonable assumptions can be made about several elements that could cause problems. These include any elements which can reduce UO_2 and add to the fuel decomposition problem discussed in section II. In addition, some elements may form low melting eutectics with UO_2 , tungsten, or both and thereby result in undesirable side reactions. Elements particularly suspect in these respects are carbon and fluorine. Therefore, attempts have been made to keep the amounts of these elements as low as possible in the tungsten and UO_2 starting materials and throughout subsequent processing.

Carbon contamination, even at levels as low as 50 ppm, has resulted in reactions with tungsten and UO_2 . Therefore, care is taken to maintain the concentration level of this element at less than 20 ppm. Although this low impurity level can be readily attained in the starting materials, additional carbon is often introduced to composites from organic binders during the fuel element fabrication process. Therefore, close control of this element must be maintained through all processing steps.

Fluorine contamination has been frequently encountered as a result of the tungsten vapor deposition process that is used to coat the UO_2 particles in some fuel element fabrication processes. The deposition process used most commonly involves hydrogen reduction of tungsten hexafluoride. However, this process occasionally has resulted in residual quantities of greater than 3000 ppm fluorine (probably present as tungsten oxyfluorides). When composites containing these fluorides were heated to high temperatures, the fluorides vaporized leaving a string of porosity along the grain boundaries of the tungsten matrix and cladding. Recent results indicate that fluoride contamination greater than about 75 ppm cannot be tolerated in W- UO_2 composites and that even lower

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) [REDACTED]

concentrations (<20 ppm) are desired.

To meet the need for high purity in W-UO₂ fuel elements for nuclear rocket applications, NASA has employed materials that are at least 99.95 percent pure with no single impurity exceeding 200 ppm. (As noted previously, carbon and fluorine concentrations are required to be even lower, less than 30 ppm). These impurity levels seem to be satisfactory; however, further study of the effects of impurities is needed to determine if even more stringent specifications are required.

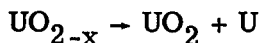
Fuel Stoichiometry

Results from several organizations have indicated that the operating lifetime of W-UO₂ composites is highly dependent upon the stoichiometry of the UO₂. Excess oxygen (O/U greater than 2.01) can result in the formation of a low-melting W-U-O eutectoid, which can degrade the core. On the other hand, oxygen deficient UO₂ (O/U less than 2.00) results in the release of free uranium, which also has a low melting point and can degrade the composite. Thus, the initial stoichiometry of the fuel must be carefully controlled.

In addition, it has been found that the stoichiometry of the fuel can change during operation of W-UO₂ composites at elevated temperatures. This can be illustrated through use of the recently published oxygen-uranium phase diagram (from ref. 6) shown in figure I-4. As indicated, heating stoichiometric UO₂ to an elevated temperature, such as 2500° C, and holding the material at this temperature level has been observed to result in loss of oxygen from UO₂ with resultant change to a substoichiometric form, as represented by the reaction



If the composites are maintained at this temperature level, the effects are not deleterious, since the UO_{2-x} remains as a single phase. However, cooling of composites leads to serious problems, for as the temperature decreases, the solvus line is crossed. This causes the UO_{2-x} to precipitate the excess uranium, as illustrated by the reaction



This precipitated uranium, which is molten at these temperatures, can migrate through the grain boundaries of the tungsten matrix, thereby weakening the structure. Continued thermal cycling of composites aggravates this problem, since each additional cycle causes more uranium to be transferred by this mechanism from the fuel to the

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tungsten matrix.

Since this reduction and disproportionation of UO_2 cannot be tolerated to any appreciable extent in reactor fuel elements, several organizations studying W- UO_2 composites have been seeking methods to circumvent the problem. Currently, the most promising method is to add small amounts of other metal oxides in solid solution with the UO_2 (ref. 7). Although the role of these oxide additives is not fully understood, they are thought to increase the thermodynamic stability of UO_2 to reduction.

Results of Lewis screening studies (ref. 8) on the effectiveness of different oxides are shown in figure I-5. This plot shows the measured fuel loss resulting from repeated thermal cycling to 2500°C of W- UO_2 composites containing UO_2 stabilized with different oxide additions (all added at the 10 mole percent concentration level). The relative effectiveness of the additives fell into the several classes shown. For comparison, a curve for composites with unstabilized UO_2 is shown at the left. The addition of TiO_2 resulted in no improvement in performance. However, all the other oxide additions improved the cyclic life of these composites. Of particular interest are the oxide additives that fell into the two most effective groups: Nd_2O_3 , Y_2O_3 , Gd_2O_3 , PrO_2 , CeO_2 . Recent results of more extensive testing of composites with some of these additives (Y_2O_3 and CeO_2 at Lewis and Gd_2O_3 at Argonne) have indicated that use of these additions can prolong the cyclic life of W- UO_2 composites to levels sufficient for space reactor use.

Although the addition of metal oxide additives to UO_2 improves the operating performance of W- UO_2 composites, these additions make the chemical analysis problems more difficult. In particular, previously established techniques for determining the fuel stoichiometry must be revalidated or modified to allow for the effects of additives on the analytical results.

CONCLUSION

Dispersions of UO_2 in tungsten appear to hold considerable potential for use in space flight reactors for either propulsion or power generation. However, the high operating temperatures required of fuel elements in these reactor systems necessitate very close control of the materials used in the reactors. In particular, high purity materials must be used, and contamination must be avoided during processing. In addition, the stoichiometry of the fuel must be controlled within narrow limits even with stabilizing oxides in the fuel. Meeting these objectives will require extensive use of chemical analysis both as a research tool in experimental programs evaluating the potential of W- UO_2 composites and as a quality control tool in the eventual production and testing of reactor fuel elements. Therefore, proven analytical techniques applicable to a wide variety of W- UO_2 compositions must be available for use.

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REFERENCES

1. Anon.: Nuclear Rocket Program. Rep. No. ANL-7150, Argonne National Laboratory, 1965.
2. Lietzke, Armin F.: Water-Moderated Tungsten Nuclear Rocket Reactor Concept. NASA TM X-1044, 1965.
3. Anon.: 710 Reactor Program, Progress Report No. 17. Rep. No. GEMP-395, Nuclear Materials and Propulsion Operation, General Electric Co., Dec. 1, 1965.
4. Anon.: Research and Development on Fission-Heated Thermionic Cells for Applications to Nuclear Space Power Systems. Rep. No. GA-6892, General Atomic Division, General Dynamics Corp., 1965.
5. Anon.: Development of a Nuclear Thermionic Fuel Element. Rep. No. GESR-2051, Special Purpose Nuclear Systems Operation, General Electric Co., 1965.
6. Martin, Allen E.; and Edwards, Russell K.: The Uranium-Uranium Dioxide Phase Diagram at High Temperatures. J. Phys. Chem., vol. 69, no. 5, May, 1965, p. 1788.
7. Garfinkel, Marvin: Effects of Additives on Thermal Stability of Tungsten-Uranium Dioxide Composites. NASA TM X-1118, 1965.
8. Saunders, Neal T.; Gedwill, Michael A.; and Gluyas, Richard E.: Retention of Fuel in Tungsten-Uranium Dioxide Fuel Elements. Paper presented at the AIAA Propulsion Joint Specialist Conference, Colorado Springs, Colorado, June 14-18, 1965. (Also available as NASA TM X-52184.)

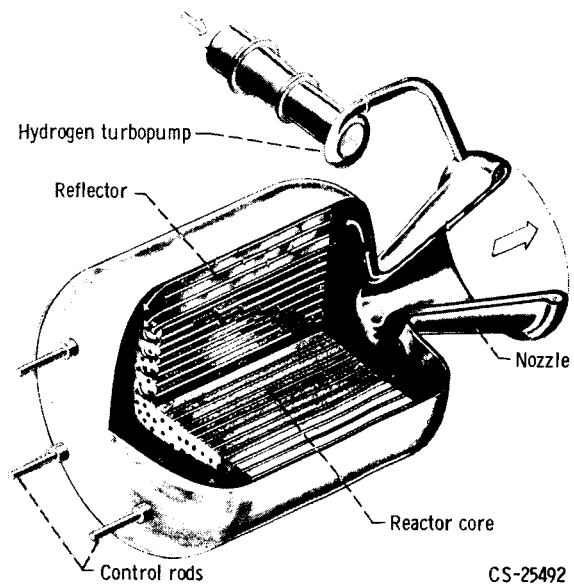


Figure I-1. - Solid core heat-transfer-type nuclear rocket.

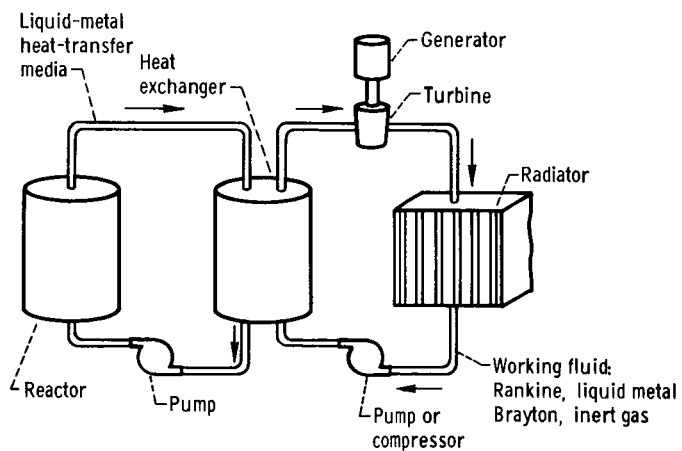


Figure I-2. - Schematic illustration of a turbogenerator-type (Rankine or Brayton cycle) space electric power system.

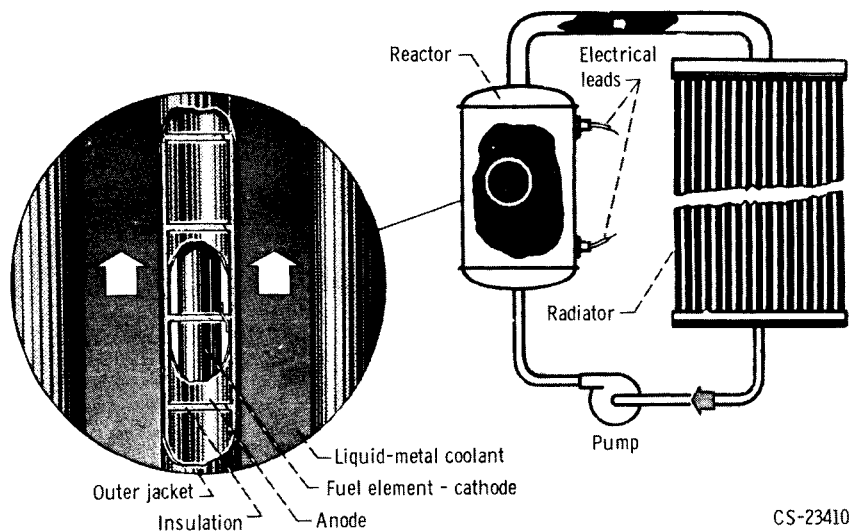


Figure I-3. - Nuclear thermionic power system.

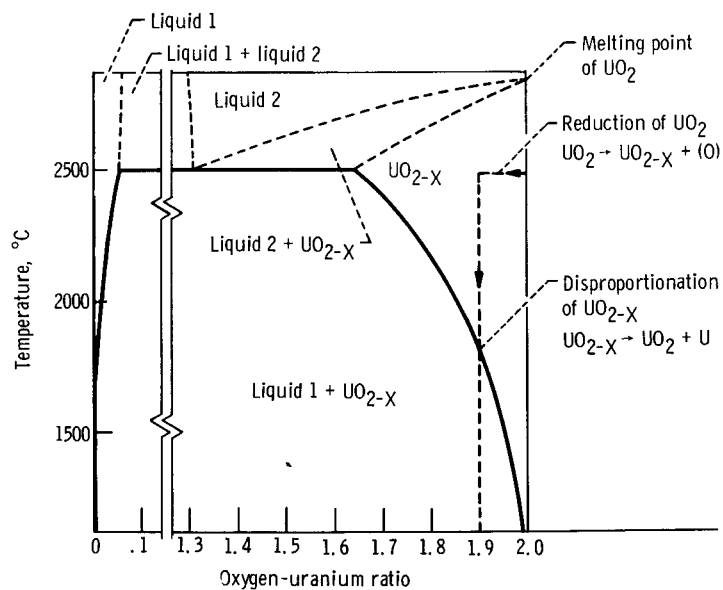


Figure I-4. - Oxygen-uranium phase diagram

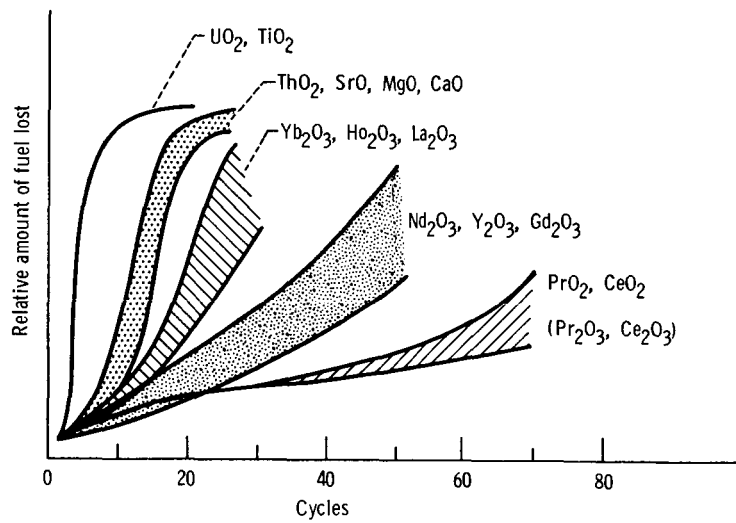



Figure I-5. - Comparison of stabilizing additives in tungsten - uranium dioxide composites. Cycle time, 10 minutes; temperature, 2500° C; environment, pure hydrogen.



II. PROGRESS TOWARD MEASURING EXCESS OXYGEN IN TUNGSTEN - URANIUM DIOXIDE CERMETS

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SUMMARY

Direct methods were developed for quantitatively measuring excess oxygen in tungsten - uranium dioxide cermets and for establishing its location. The technique is based on quantitative measurement of the products from sequential gaseous reductions of the cermet, using (1) carbon monoxide removal of the hyperstoichiometric oxygen of the uranium dioxide and (2) hydrogen removal of the oxygen associated with tungsten.

Preliminary experiments indicate that gaseous reduction techniques may also be applicable to the measurement of available oxygen in Y_2O_3 (or CeO_2) stabilized tungsten - uranium dioxide cermets.

X-ray fluorescence techniques for determining uranium and stabilizer contents were developed and applied to both thermally cycled and noncycled cermets.

INTRODUCTION

Tungsten - uranium dioxide cermets have numerous characteristics which make them desirable as fuel materials for high-temperature nuclear reactors (refs. 1 and 2). One of the major problems associated with their use is their inability to retain the fuel material (UO_2) during thermal cycling (ref. 3). Battelle-Northwest is presently studying the mechanism of this fuel loss in an effort to improve the cermet performance (refs. 4 and 5). Thermal cycling data have been accumulated which indicate that the fuel loss mechanism is related to the excess oxygen content of the fuel (that above the amount necessary to form stoichiometric uranium dioxide) (unpublished data obtained by J. L. Daniel and R. J. Baker of Battelle-Northwest). Hence, it has become of particular interest to determine the quantity of excess oxygen and its location: that is, whether it is present as hyperstoichiometric uranium dioxide or as an oxide of tungsten.

Many methods have been published for the determination of the stoichiometry of uranium dioxide. The more widely accepted of these include

- (1) Dissolution in a nonoxidizing medium followed by redox or electrochemical titration of the U(VI) present (refs. 6 to 8)
- (2) High-temperature thermogalvanic measurements (refs. 9 and 10)
- (3) Thermogravimetric measurements coupled with oxidation (refs. 11 and 12)
- (4) X-ray diffraction techniques (ref. 13)
- (5) Gaseous reduction techniques (refs. 14 and 15)

The presence of the large amount of tungsten metal in the cermets markedly restricts the use of most of the above methods. In both the redox titration and thermogalvanic methods, the reducing properties of the tungsten will mask the measurement completely. In the thermogravimetric and X-ray diffraction methods, the large mass and high atomic number of the tungsten reduces the precision of the method so drastically that prohibitively exacting techniques are required to obtain adequate determinations. The gaseous reduction approach, on the other hand, measures the quantity of interest, namely, the oxygen which is in excess of that necessary to form stoichiometric uranium dioxide. The method has been proven to be quantitative and to have sufficient sensitivity in the case of oxide samples. This paper describes the progress to date on the development of a procedure which also makes it selective and therefore permits the determination of both quantity and location of the excess oxygen in tungsten - uranium dioxide cermets.

This report is based on work performed under United States Atomic Energy Commission Contract AT(45-1)-1830 and was carried out in close collaboration with J. L. Daniel and R. J. Baker of the Ceramics Research and Development Section. The author is indebted to D. A. Nissen for the thermogravimetric measurements, and to W. O. Greenhalgh and F. T. Hara for the development and application of the X-ray fluorescence determination for total uranium.

EXPERIMENTAL

As a first step in defining the conditions under which specificity could be achieved, thermobalance reductions were made on uranium dioxide of known stoichiometry and on tungsten of known oxygen content using both carbon monoxide and hydrogen as reductants. Thermobalance reductions were restricted, by the nature of the available apparatus, to flowing streams of explosion-proof gas at atmospheric pressure. Therefore, the conditions to be used later in the gas handling system could not be exactly defined. Under the conditions available, carbon monoxide and hydrogen reductions of uranium dioxide with an oxygen-uranium ratio of 2.025 and of tungsten dioxide were carried out. Carbon

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monoxide reduction of the uranium dioxide commenced at about 510°C and was complete at 670°C . Carbon monoxide did not significantly alter the weight of tungsten dioxide below 1000°C . Hydrogen reduction of the uranium dioxide started at about 600°C and was complete at about 730°C , while the hydrogen reduction of tungsten dioxide started at about 750°C and was complete at about 900°C . Thus, it can be seen that a wide range of conditions exists under which carbon monoxide will quantitatively reduce hyperstoichiometric uranium dioxide without altering the oxygen content of the tungsten significantly. A similar but narrower range exists for hydrogen reduction. Based on these results and the results of a large number of reductions carried out under fixed conditions in the gas handling system, the following procedure was developed to determine the oxygen-to-uranium ratio of the uranium dioxide contained in a cermet:

- (1) The sample is weighed in a platinum boat and placed in the furnace tube of the gas handling system. If sufficient sample is available, about 2 grams are usually taken.
- (2) The sample is dried under vacuum by heating to 600°C for 15 minutes.
- (3) The sample is cooled, and carbon monoxide is admitted to the system until the pressure reaches about 180 millimeters of mercury.
- (4) The reduction is carried out by heating the sample to 600°C for 15 minutes in this atmosphere of circulating carbon monoxide. (The carbon dioxide formed should not be removed from the carbon monoxide stream as long as the unknown is hot, because it suppresses the carbon monoxide disproportionation reaction.)
- (5) The unknown is cooled, and the carbon dioxide is removed from the circulating gas with a liquid-nitrogen trap.
- (6) The carbon monoxide is pumped off.
- (7) The trap is warmed, and the carbon dioxide is measured manometrically.

The hyperstoichiometric oxygen content of the sample can be calculated from the measured quantity of CO_2 . This number coupled with the uranium content of the sample (its determination will be discussed shortly) can be used to calculate the oxygen-uranium ratio of the cermet.

After carbon monoxide reduction, the oxygen remaining in the cermet is either present as stoichiometric uranium dioxide or an oxide of tungsten. Under the proper conditions, hydrogen will quantitatively remove the oxygen from tungsten oxides without affecting stoichiometric uranium dioxide. Therefore, the tungsten oxide content of a cermet may be determined on the carbon monoxide reduced sample by the following procedure:

- (1) After the removal of the carbon dioxide from the system, hydrogen is admitted to a pressure of about 180 millimeters of mercury.
- (2) Reduction is carried out by heating the sample in a circulating stream of hydrogen for 90 minutes at 800°C . The stream is circulated through the liquid-nitrogen trap to continuously remove any water formed.

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(3) The sample is cooled, and the hydrogen is removed from the system.

(4) Helium is admitted to a pressure of 180 millimeters of mercury and circulated between the cold trap and the electrolytic P_2O_5 cell.

(5) The cold trap is warmed, and the water is titrated coulometrically as it is carried into the electrolytic cell.

(6) The oxygen content of the tungsten can be calculated directly from the measured water value.

To relate the hyperstoichiometric oxygen numbers to an oxygen-uranium ratio, one must also know the uranium content of the sample. The most difficult task in performing a total uranium determination on a tungsten - uranium dioxide cermet is to achieve complete dissolution of the sample. A procedure was developed for this analysis based on placing the sample in solution by pyrosulfate fusion followed by the X-ray fluorescence determination of the uranium directly on the melt. It may be outlined as follows:

(1) Approximately 0.2 gram of powdered sample is accurately weighed into a porcelain boat, and approximately 2 grams of potassium pyrosulfate and a carefully measured amount of internal standard (strontium) are added.

(2) Approximately 2 milliliters of concentrated sulfuric acid are added, and the sample is heated slowly on the hot plate until the majority of the particles are dissolved. (The sulfuric acid addition may have to be repeated.)

(3) The mixture is fused over a Meker burner until a clear yellow melt is obtained.

(4) The melt is cooled and ground, and a portion is mounted for X-ray fluorescence measurements.

(5) The intensity ratios of the following lines, $U\text{ }L\alpha_1$, $Sr\text{ }K\alpha$, and $Y\text{ }K\alpha$, are measured using a Norelco X-ray fluorescence spectrometer and a tungsten target tube operated at a 50-kilovolt peak and 40 milliamperes current. A LiF analyzing crystal, scintillation detector, and a pulse height discrimination are used.

(6) The uranium and additive (yttrium or cerium) concentrations are calculated.

The function and even the desirability of the drying step in the oxygen-uranium ratio determination is open to some debate, particularly considering the fact that a high vacuum is not maintained with the system. It should be studied more completely. However, this operation has provided some valuable information in the case of thermally cycled cermets. Significant quantities of gas were released from these specimens during this operation, and a correlation was found to exist between the quantity of gas released and the number of thermal cycles which the cermet had undergone. The interpretation of this correlation has contributed to the development of a theory as to the fuel loss mechanism (unpublished data obtained by J. L. Daniel and R. J. Baker of Battelle-Northwest).

The particular temperature and duration of the carbon monoxide reduction were selected to insure a complete reduction, to insure selectivity, and to maintain the blanks

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at acceptable levels. Blanks arise from the disproportionation of carbon monoxide to carbon and carbon dioxide on the hot surface of the cermet. Short reduction times, low reduction temperatures, and small sample surface areas all help to minimize the blank.

The quantities of water involved in the tungsten oxide determination by reduction with hydrogen are small (50 to 500 μg), and unusual techniques are required for their accurate measurement. A complete description of the technique would constitute a paper in itself and can only be summarized here. A conventional P_2O_5 electrolytic hydrometer cell is black-waxed directly into the glass system and electrically connected to a direct current power supply and current integrator. The current integrator used in these studies was a conventional operational amplifier-capacitor circuit (ref. 16) using a Dymec Model 2460A operational amplifier. The readout can be either a digital voltmeter or a recorder.

The gas handling system used in this work is shown in line diagram form in figure II-1. One of the major problems associated with the quantitative measurement of small quantities of water in a gas handling system is adsorption of the water on the walls of the system. In the titrations described in this paper, a dynamic equilibrium exists which should be studied more completely when time permits. In fact, more complete understanding or control will be absolutely necessary if it is ever desired to go below the 50-microgram level. However, all the data collected to date indicate that the equilibrium is sufficiently reproducible to permit satisfactory operations in the range of present interest (namely, from 50 to 1000 μg of water per titration), and, therefore, an extended study of the equilibrium has not been made.

The limiting factor in both the carbon monoxide and the hydrogen reductions is the blank size. If it is assumed that a 2-gram sample of 10 to 20 weight percent uranium dioxide is used, variations from stoichiometry of about 0.002 oxygen-uranium-ratio units can be detected with a precision of about ± 0.002 unit with the present operating procedure and blanks. Oxygen in tungsten can be detected at about the 10-ppm level with a precision of about ± 5 ppm.

In work such as this, one always questions the completeness of the gas-solid reaction. To insure completeness and speed, the original work was done on powdered and screened samples. (The entire sample was powdered to pass through a 100-mesh screen.) Most of the samples were powdered in air. This, of course, raises the question of reaction of the sample with air during the sample preparation step. Several pieces of evidence exist which indicate that such exposure does not significantly increase the oxygen content of our samples. These are as follows:

- (1) Samples of low-oxygen heliarc tungsten which were powdered in this manner do not exhibit a detectable oxygen content.
 - (2) Two portions of a given cermet sample, powdered to different mesh sizes, exhibit the same apparent oxygen content.
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(3) The oxygen pickup of a powdered sample has been measured as a function of time over a period of several days and is shown in figure II-2. The rate of pickup is too slow to add a significant amount of oxygen to the sample if it is analyzed within the first few hours. This does not exclude the possibility that a significant pickup occurred as the new surface was formed during powdering.

In spite of this evidence, it was felt that significant hazards were involved in powdering samples in air. The hazards can be eliminated either by performing the entire sample handling operation in an inert atmosphere or by performing the reductions on massive cermet pieces. After reviewing the work of J. O. Hibbits (unpublished data from General Electric, Nuclear Materials and Propulsion Operation) on the measurement of uranium metal in cermets by hydriding techniques, it was decided to attempt reductions on massive cermet samples. After running many such pieces, the author feels that realistic values for oxygen-uranium ratios and tungsten oxide content are obtained. This has not been proven completely to the author's satisfaction, however, because all the pieces (except one) analyzed to date have shown stoichiometric oxygen-uranium ratios. Either the fabrication procedures used always produce cermets with stoichiometric uranium dioxide (which is probable), or the carbon monoxide is not reaching the oxide in the massive pieces. A massive cermet piece containing uranium dioxide of known sub-stoichiometric oxygen-uranium ratio should be run if such a piece can be obtained.

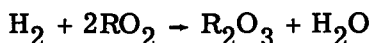
In the area of tungsten - uranium dioxide cermets containing additives, only some very preliminary experiments have been performed, but they show that the approach holds promise of providing useful information. If a sample of mixed oxide is "analyzed" or put through the procedure described above, the following facts are soon evident:

(1) The carbon monoxide reduction does not remove a significant amount of the oxygen.

(2) The hydrogen reduction does remove a significant and reproducible amount of the oxygen from these mixed oxides.

(3) This removal is not instantaneous (see fig. II-3). Note that there appear to be two distinct slopes to the curve suggesting the possibility of the reduction of two distinct species.

(4) Beales and Handwerk (ref. 17) at ANL have shown the oxygen-metal ratio of gadolinium-containing uranium dioxide in the range of 0 to 40 mole percent gadolinium to be 2.00. The uncertainties in the meager hydrogen reduction data obtained in the present investigation on yttrium-containing uranium dioxide are too large to permit firm conclusions regarding the stoichiometry of the mixed oxide, but the data show some evidence that only about 80 percent of the oxygen necessary for the completion of the reaction



is being released.

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The work to date on the analysis (by gaseous reduction) of mixed oxides and cermet containing mixed oxides has created more questions than it has answered. Some of the areas which are believed to be worthy of further investigation are

(1) An attempt should be made to define what is called "available oxygen" the reproducible quantity of oxygen which the hydrogen removes.

(2) A search for some correlation of the quantity of available oxygen, the rate of its release, or the temperature of its release with fuel retention ability should be made.

(3) Attempts should be made to develop an analytical method which is specific for the various forms of oxygen in a cermet containing mixed oxides. Scouting experiments using reductions on a thermobalance similar to those described earlier in this document could be used as the initial step.

(4) Attempts should be made to interpret the reduction rate curves to identify the two species present and to aid in the understanding of the mechanism of additive action.

REFERENCES

1. Lietzke, A. F., Water-Moderated Tungsten Nuclear Reactor Concept. NASA TM X-1044, 1965.
2. Saunders, N. T., Watson, G. K., and Buzzard, R. J., Investigation of Tungsten and Uranium Dioxide as a Nuclear Rocket Fuel Material. Proc. Nucl. Prop. Conf., Monterey, California. TID 7653 Pt. II-Book 2, pp. 454-462, 1962.
3. Reactor and Fuels Laboratory Quarterly Report on Cermet Research and Development Activities, HW-84611 and NASA CR-54229, July, Aug., Sept. 1964.
4. Reactor and Materials Technology Department Quarterly Report on Tungsten-Uranium Dioxide Cermet Research and Development Activities, BNWL-39 and NASA-CR-54304, Nov. and Dec. 1964.
5. Reactor and Materials Technology Department Quarterly Report on Tungsten-Uranium Dioxide Cermet Research and Development Activities, BNWL-110 and NASA-CR-54409, Jan. - March 1965.
6. Shalgosky, H. I., Smart, R. C., and Watting, J., The Precise Determination of O/U Ratios in Uranium Dioxide by Comparative Polarography, AERE-R-4270, June 1964.
7. Burn, R. M., and Goward, G. W., The Polarographic Determination of Hexavalent Uranium in Uranium Oxides (The Determination of Oxygen/Uranium Ratios) WAPD-205, April 1959.

8. Stromatt, R. W., and Connally, R. E., Determination of the Stoichiometry of Uranium Dioxide by Controlled Potential Coulometry. Analytical Chemistry, Vol. 33, p. 354, March 1961.
9. Markin, T. L., and Bones, R. J., The Determination of Changes in Free Energy for Uranium Oxides Using a High Temperature Galvanic Cell, AERE-4042, Part 1, 1962.
10. Markin, T. L., and Bones, R. J., The Determination of Some Thermodynamic Properties of Uranium Oxides with O/U Ratios Between 2.00 and 2.03 Using High Temperature Galvanic Cell, AERE-R-4178.
11. Stonhill, L. G., The Determination of Atomic Ratios in the Uranium-Oxygen System by a Thermogravimetric Method. Canadian Journal of Chemistry, Vol. 37, pp. 454-459, 1959.
12. Lyon, W. L., The Measurement of Oxygen to Metal Ratio in Solid Solutions of Uranium and Plutonium Dioxides, GEAP-4271, 1963.
13. Young, W. A., Lynds, L., Mohl, J. S., and Lebowitz, G. G., An X-Ray and Density Study of Non-stoichiometry in Uranium Oxides, NAA-SR-6765, 1962.
14. Roberts, L. E. J., and Harper, E. A., The Determination of Oxygen in Uranium Oxides, AERE-C/C-885, 1952.
15. Markin, T. L., Walter, A. J., and Bones, R. J., The Determination of Oxygen/Metal Ratios for Uranium, Plutonium and (U, Pu) Oxides, AERE-R-4608, 1964.
16. Booman, G. L., Instrument for Controlled Potential Electrolysis and Precision Coulometric Integration, Analytical Chemistry, Vol. 29, p. 213, 1957.
17. Beals, R. J., and Handwerk, J. H., Solid Solutions in the System Urania - Rare Earth Oxides: I. $\text{UO}_2\text{-GdO}_2$, Journal of the American Ceramic Society, Vol. 48, No. 5, pp. 271-274. May, 1965.

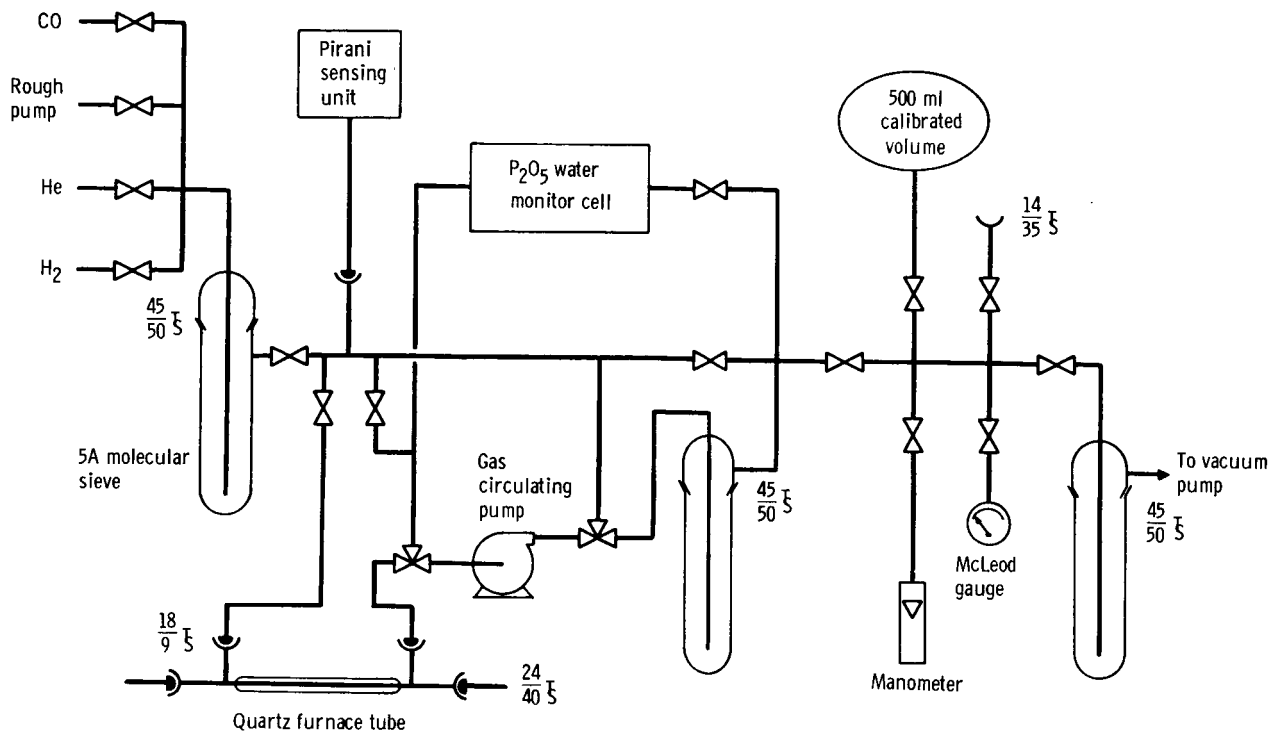


Figure II-1. - Gas handling system.

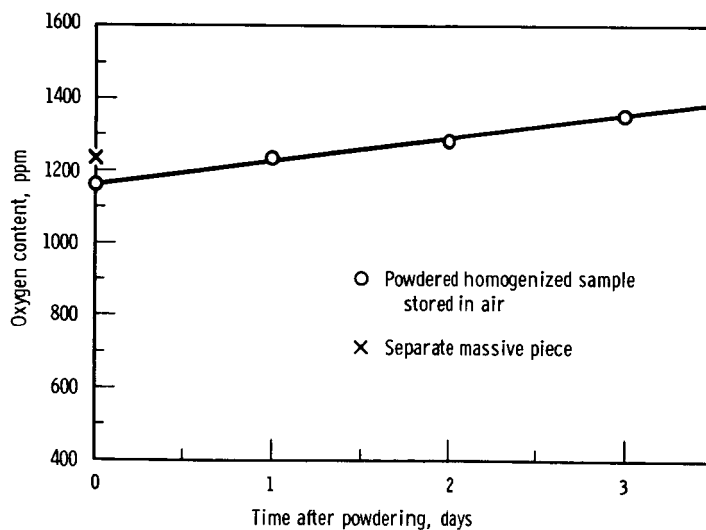


Figure II-2. - Uptake of oxygen by powdered cer met.

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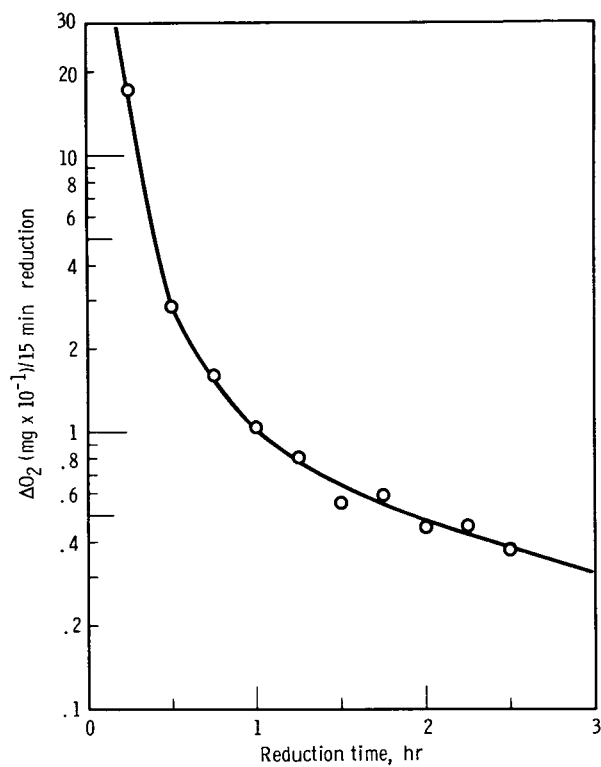


Figure II-3. - Rate of oxygen removal from mixed oxide ceramics.

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III. DETERMINATION OF URANIUM AND THORIUM METAL IN FUEL ELEMENT CORE MATERIALS

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SUMMARY

A method is reported for the determination of uranium and/or thorium metal in sintered UO_2 , ThO_2 , $\text{UO}_2\text{-ThO}_2$, or W-UO_2 specimens, subject to certain qualifications. The method of determination involves the formation of the metal hydrides UH_3 and Th_4H_{15} and their selective decomposition. At 325°C , UH_3 decomposes to U and H_2 , and Th_4H_{15} decomposes to ThH_2 and H_2 . At 600°C , ThH_2 decomposes to Th and H_2 . The hydrogen released by decomposition is determined by gas chromatography.

The accuracy of the determination is limited by the location of the metallic phase(s) present. In general, metal located along a grain boundary will react with hydrogen and subsequently can be determined, whereas metal located within a grain will probably not hydride and thus will escape subsequent detection.

The method is not applicable to Mo-UO_2 specimens because of the solubility of uranium metal in molybdenum. A high molybdenum - low uranium alloy does not hydride to any appreciable extent under the conditions outlined in this paper.

INTRODUCTION

Metallic uranium has been identified in specimens of uranium dioxide after heating at temperatures near or above 2000°C in either inert or reducing atmospheres (refs. 1 to 5). Rothwell (ref. 2) has proposed that the "free" uranium metal appears as a result of precipitation of the metal from substoichiometric UO_{2-x} phase during the cooling cycle. Investigations at General Electric-Nuclear Materials and Propulsion Operation (GE-NMPO) by Aitken et al. (refs. 5 and 6) have indicated that a congruent vaporization composition (dependent upon temperature and oxygen partial pressure) with an oxygen-

uranium ratio of approximately 1.88 can be reached.

Inasmuch as a number of different fuel core materials are being investigated under conditions which could lead to the formation of "free" uranium metal, it becomes important to determine the amount of metal formed as a result of various treatments.

Lyon (ref. 7) has reviewed some of the potentially useful methods for such a determination and has indicated that the most promising technique was oxidation to U_3O_8 . We have found that oxygen-uranium ratios accurate to about ± 0.002 unit can be attained if 5- to 10-gram samples are used. Although this technique is satisfactory for UO_2 samples,¹ it is unsuitable for samples of W- UO_2 or Th O_2 - UO_2 because the composition of the ignited oxides can vary with temperature and time of ignition.

An attractive method for the determination of "free" uranium metal in a W- UO_2 fuel core is the technique of hydriding and dehydriding the metal.² After appropriate evacuation, the sample is heated in a hydrogen atmosphere and then cooled to room temperature. After reevacuating the system, the sample again is heated to decompose the hydride. The hydrogen is removed from the system by means of a Toepler pump, collected, and determined by gas chromatography.

This technique appears to be feasible for the following reasons:

(1) Mulford, Ellinger, and Zachariasen (ref. 8) have reported that hydrogen-uranium ratios of 2.94 to 3.00 are obtained when massive uranium metal is hydrided. The present authors have obtained values of 3.00 within experimental error using the procedure to be described.

(2) Gueron and Yaffee (ref. 9) have reported that UH_3 is formed in 2 hours at $250^\circ C$, in 5 hours at $150^\circ C$, in 24 hours at $100^\circ C$, and in 2 weeks at $20^\circ C$. Concerning the reaction of hydrogen with uranium metal, Wilkinson (ref. 10) states that "the rate of reaction with uranium is most rapid - about 0.2 to 0.3 centimeter penetration per hour - at temperatures near $225^\circ C$, but it declines rapidly with increases of temperature above $250^\circ C$ and becomes zero when the dissociation pressure equals the external hydrogen pressure (approx. $432^\circ C$)."

(3) The literature is rather noncommittal concerning the stability of UO_3 at room temperature in a vacuum. The authors have found that if a system containing UH_3 is evacuated to about 10 microns at room temperature and then sealed, the pressure does

¹Henceforth, UO_2 refers to any or all the following: UO_{2-x} , $UO_{2.000}$, and UO_{2+x} . Each of the individual types of compositions will be appropriately indicated.

²Recent results from the application of this method for the determination of yttrium metal in yttria and for the simultaneous determinations of uranium and yttrium metals in UO_2 - Y_2O_3 specimens are presented in the appendix to this paper.

1 [REDACTED]

not increase significantly in 30 minutes. S. Kallmann (private communication from Ledoux and Co.) has reported that this stability exists in a vacuum of < 1 micron.

(4) The literature indicates that UO_3 decomposes at temperatures near 400°C . The authors have found that UH_3 decomposes at much lower temperatures if a vacuum is maintained. Complete decomposition was obtained at 300°C in about 20 minutes, with no significant difference in results when the decomposition was carried out at 800°C .

The authors gratefully acknowledge N. P. Fairbanks, R. E. Fryxell, C. S. Wukusick, and W. R. Yario for specimen preparation; C. A. Asaud and F. T. Williams, Jr., for metallographic examination; D. K. Conley for electron microprobe examination; and P. F. Elliot and A. F. Rosenberg for some of the hydride analyses.

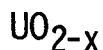
This paper originated from work sponsored by the Fuels and Materials Development Branch, Atomic Energy Commission, under Contract AT(40-1)-2847.

EXPERIMENTAL

The sample, contained in a small platinum boat, was transferred to a 1-inch-diameter Vycor combustion tube. The system was evacuated, flushed with "ultrapure" hydrogen, and reevacuated to about 10 microns of mercury. The system was sealed and hydrogen (approx. 1 atm) was admitted. The sample was then heated to 225°C , and this temperature was maintained for 4 to 5 hours. (Although it has been established that this time is sufficient to hydride the accessible uranium metal in the sample, it has not been established that this much time is needed.) The sample was cooled to room temperature, and the system was evacuated (to approx. 10 microns of mercury). The system was sealed again and heated to 600°C . The hydrogen released was transferred by means of a Toepler pump to a gas collecting bulb. An aliquot of this gas was analyzed by gas chromatography. The apparatus used is shown in figure III-1.

After establishment of the utility of the method, another apparatus was constructed for adding hydrogen to the tubes, and the apparatus shown was used only for hydride decomposition. Separate tube furnaces were used for the hydriding treatment. This combination enables one person to analyze 12 samples in an 8-hour working period.

RESULTS



Before applying the hydriding method to more complex samples, it was decided to apply the method to the determination of free uranium metal (and consequently the

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oxygen-uranium ratio) in UO_{2-x} . In this manner, the results could be evaluated by comparison with those obtained by the method of oxidation (to U_3O_8). The results obtained initially, using the "hydriding" technique, were confusing in that some results agreed very well with those obtained by the oxidation method, whereas other results were significantly low (with respect to the amount of uranium metal present). It has been established that the results can be explained on the basis of the location of the uranium metal in the sample. Photomicrographs of typical sintered specimens of UO_{2-x} are shown in figures III-2 and III-3 together with oxygen-uranium values obtained by both analytical techniques.

The uranium metal in the agglomerated³ fuel system (fig. III-2) is located almost entirely on the grain boundaries, whereas, in the as-received specimen (fig. III-3) a significant amount of free metal is located within the grain. It is assumed that hydrogen can both react with and be evolved from uranium located along a grain boundary, whereas it would take a very long time for hydrogen to diffuse through the grain at 225°C and react with an intragranular uranium particle. The utility of this method, therefore, depends on correlation with sample microstructure. Some typical results obtained using this technique are shown in table III-I.

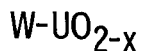
The results shown in table III-I strongly suggest that the UO_{2-x} samples tested consist of $\text{UO}_{2.000}$ and uranium metal. Examination of sample photomicrographs and correlation with the free uranium metal results indicate that very good agreement (with oxidation results) is obtained when the uranium metal is located along a grain boundary. This agreement would be good only if the oxide phase were $\text{UO}_{2.000}$ (or something very close to this value).

It might also be pointed out that uranium metal has never been found (by electron microprobe examination) in any UO_2 sample with an oxygen-uranium ratio greater than 2.00. This statement obviously applies only to the authors' laboratory.

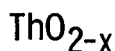
There is a rather small "blank" obtained using this technique which amounts to approximately 0.15 milliliters of hydrogen. The effect of the correction depends upon the amount of sample analyzed (and its surface area) and the amount of metal present. For example, a sample containing 0.5 percent uranium metal has an oxygen-uranium ratio equal to 1.988. The blank correction on a 5-gram sample amounts to about 0.2 percent uranium, which does not significantly change the calculated oxygen-uranium ratio.

³Agglomerated UO_2 : as-received UO_2 isostatically pressed at 70 000 psi. The pressed cake is crushed and sieved. The -100 +200 mesh particles are fired at 750°C in helium for 1 hour.

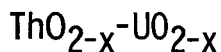
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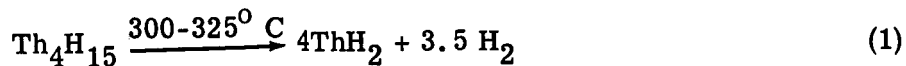
At the present time, there is no way of checking the accuracy of the hydriding method when applied to W-UO_{2-x} samples. However, until proven otherwise, we shall postulate that the same oxygen-uranium ratio would be obtained in a W-UO_2 sample as would be obtained in UO_2 if they were both sintered under identical conditions. Consequently, the applicability of the hydriding technique has been evaluated by comparing the results obtained on W-UO_{2-x} samples with those obtained on UO_{2-x} control samples (the two materials sintered simultaneously). Typical results are shown in table III-II and indicate the applicability of the technique.



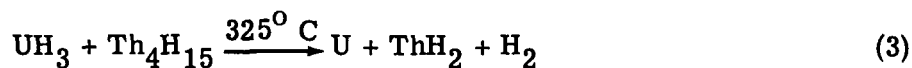
Thoria can become substoichiometric in a manner similar to uranium dioxide, also leading to the formation of free metal during the cooling cycle. The authors have found that if thorium metal is hydrided (225°C) and dehydrided (600°C) using the same conditions described for uranium, an amount of hydrogen is found equivalent to a hydride composition of Th_4H_{15} , in agreement with the literature. Using this technique, the thorium metal values in ThO_{2-x} obtained by the hydriding method were always low in comparison to oxidation results. This is to be expected on the basis of the observed microstructure such as the one shown in figure III-4 in which a significant amount of metal is seen within the grains.



During the determination of thorium metal in the above specimens, the evolution of hydrogen in the dehydriding step appeared to be proceeding stepwise. Investigation, as shown in table III-III, indicated that the following reactions were taking place:



The simultaneous determination of metallic uranium and metallic thorium should be possible merely by lowering the dehydriding temperature for uranium from 600° to 325°C .



Typical values obtained in tests of equations (3) and (4) are indicated in table III-IV.

Uranium and thorium metal values obtained in the analyses of tantalum canned UO_{2-x} - ThO_{2-x} sintered compacts are shown in tables III-V(a) and III-V(b). (The tantalum can prevents fuel depletion on the surface of the pellets which would normally occur as a result of the difference in vaporization rates of the two components.) At the present time, we have no alternate method of analysis. It should be pointed out, however, that the reported values may be low to the extent that "free" metal is located within the grains. The characteristic dispersion of spherical voids (associated with agglomerated UO_2) and the clustering of small metallic particles (associated with as-received UO_2) in UO_{2-x} - ThO_{2-x} specimens is shown in figures III-5 and III-6. The unusual nature of the structure and location of the free metal is shown more vividly in figure III-7.

Mo- UO_{2-x}

An attempt was made to apply the hydriding technique to the determination of uranium metal in sintered Mo- UO_2 specimens. The results are shown in table III-VI. Electron microprobe examination of these specimens showed no free uranium metal. However, there was an abundant third phase, consisting of a low uranium content - molybdenum alloy. The uranium concentration in the alloy was found to be about 2.5 to 4.0 percent, which is consistent with the solubility of uranium in molybdenum as indicated in the uranium-molybdenum phase diagram (ref. 11).

The above results suggested that during the sintering of a Mo- UO_2 specimen, approximately the same amount of uranium metal is formed as would normally result in the absence of molybdenum. However, on cooling, the "precipitated" uranium metal appears to dissolve in the molybdenum, forming a low uranium alloy, which in turn yields low results when hydrided.

In order to verify this hypothesis, arc-melted buttons were prepared with a composition of 4-, 40-, and 90-weight-percent uranium in molybdenum. The apparent uranium content of these buttons as determined by the hydriding technique was found to be 0.04-, 0.20-, and 92-percent uranium, respectively. It, therefore, appears that the preceding hypothesis is correct.

Concluding Remarks

The hydriding technique, subject to certain qualifications, is capable of determining the uranium metal content in UO_{2-x} and W-UO_{2-x} specimens. The method is also capable of distinguishing between uranium and thorium metal, which enables one to determine simultaneously the uranium and thorium metal contents in $\text{ThO}_{2-x}\text{-UO}_{2-x}$ specimens.

The accuracy of a metal determination in the aforementioned types of fuels appears to be limited only by the location of the uranium and/or thorium metal present. In general, metal located along a grain boundary will react with hydrogen and subsequently be determined, whereas metal located within a grain will probably not hydride and will escape subsequent detection.

The method is not applicable to Mo-UO_{2-x} specimens because of the solubility of uranium metal in molybdenum. A high molybdenum - low uranium alloy does not hydride to any appreciable extent under the conditions outlined in this paper.

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APPENDIX

Determination of Uranium and Yttrium Metal in Sintered $\text{UO}_2\text{-Y}_2\text{O}_3$ Specimens - A Tentative Method

As indicated in the Introduction of this paper, the formation of substoichiometric uranium dioxide at temperatures near or above 2000°C in either inert or reducing atmospheres and the subsequent precipitation of "free" uranium metal from the substoichiometric UO_{2-x} phase during the cooling cycle are adequately documented. A similar phenomenon has been noted when yttria specimens are sintered in hydrogen at high temperatures (private communication from W. C. Yario, GE-NMPO). Conceivably, sintered $\text{UO}_2\text{-Y}_2\text{O}_3$ specimens then could contain uranium and yttrium metal after sintering. A method that could measure the amount of each metal formed therefore is desirable.

The air oxidation of a Y_2O_{3-y} specimen to constant weight at 950°C will permit the determination of yttrium metal. However, the method is unsuitable for $\text{UO}_{2-x}\text{-Y}_2\text{O}_{3-y}$ specimens because the final composition of the ignited oxide cannot be predicted with certainty because of solid solution formation.

The "hydriding-dehydriding" technique (described in the main body of this paper and in ref. 12) for the determination of free uranium metal in sintered UO_2 appeared attractive if the selective decomposition of uranium and yttrium hydrides could be achieved. In this technique, the hydride is decomposed under vacuum at a fixed temperature, and, the hydrogen evolved is collected and determined by gas chromatography. The feasibility of this approach was indicated by the following:

(1) J. O. Hibbits and E. A. Schaefer (ref. 12) demonstrated that uranium metal hydrided to UH_3 at 225°C under 1-atmosphere hydrogen and that dehydriding of UH_3 was complete at 325°C in a vacuum.

(2) H. E. Flotow, O. W. Osborne, and K. Otto (ref. 13) reported the preparation of YH_2 from yttrium metal by hydriding at 400°C under 1-atmosphere hydrogen.

(3) H. E. Flotow, et al. (ref. 14) prepared YH_3 from YH_2 by reacting the latter with hydrogen (350 mm Hg) at 200°C .

EXPERIMENTAL

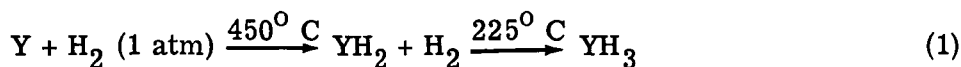
Specimen hydriding-dehydriding was carried out in the apparatus described in the main body of this paper and shown in figure III-1. In this apparatus, the sample contained in a small platinum boat was placed in a 1-inch-diameter Vycor combustion tube. The tube was evacuated to about 10 microns and then sealed with about 1-atmosphere ultra-pure hydrogen. The sample then was heated at the appropriate temperatures to form the

hydrides after which the tube was cooled to room temperature and again evacuated to about 10 microns. The tube (and the hydrided specimens) was sealed to the dehydriding system, and the system dehydrided at the appropriate temperatures. The hydrogen released at each temperature was transferred by means of a Toepler pump to a gas collecting bulb. An aliquot of this gas was analyzed by gas chromatography.

RESULTS

Yttrium Metal

"Sponge" yttrium metal was reacted with 1-atmosphere hydrogen at 450° C for 16 hours after which the temperature was lowered to 225° C and the reaction continued for abother 4 hours. Dehydriding was carried out at 450° and 950° C. The typical values of the stepwise decomposition of YH₃, shown in the following table, indicate that these reactions have taken place:

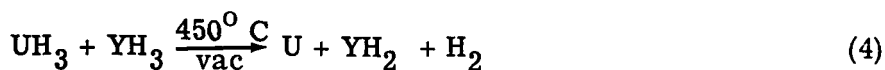


| Y, mg | H ₂ recovered (reaction (2)), percent | H ₂ recovered (reaction (3)), percent |
|----------|---|---|
| 44.1 | 101 | 101 |
| 44.1 | 102 | 96.1 |
| 45.3 | 101 | 99.1 |
| 41.4 | 101 | 99.6 |
| 48.2 | 99.6 | 100 |

Uranium Metal and Yttrium Metal

As the hydriding (225° C) and the dehydriding (450° C) of uranium metal occurs within the temperature ranges applied to yttrium metal, the possibility of the simultaneous

determination of metallic uranium and metallic yttrium is indicated by the following reactions:



Typical values of the stepwise decomposition of $\text{UH}_3 - \text{YH}_3$, obtained in tests of reactions (4) and (5), are indicated in the following table:

| U, mg | Y, mg | U found (reaction (4)), mg | Y found (reaction (5)), mg |
|----------|----------|-------------------------------|-------------------------------|
| 26.9 | 25.8 | 28.1 | 25.3 |
| 20.0 | 33.8 | 18.9 | 33.9 |

Uranium-Yttrium Alloy

Whether free metal formation within a sintered $\text{UO}_2 - \text{Y}_2\text{O}_3$ specimen will produce discrete metallic uranium and metallic yttrium particles and/or a metallic alloy of uranium and yttrium has not been established. The hydriding-dehydriding characteristics of three U-Y alloys are shown in the following table of the stepwise decomposition of hydrided uranium-yttrium alloy. The values in this table (based on reactions (4) and (5) indicate that the method is applicable to the alloy.

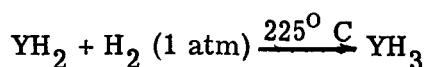
| Alloy composition, percent | Uranium determined, percent | Yttrium determined, percent |
|-------------------------------|--------------------------------|--------------------------------|
| IU-99Y | (a) | 98.9 to 99.7 |
| 50U-50Y | 49 | 50 |
| 99U-1Y | 98 | (a) |

^aPrecision of method does not permit distinguishing of individual metals in 99:1 ratio.

Crystal Bar Yttrium

Attempts to hydride crystal bar yttrium metal at 450°C and then at 225°C to yield

the trihydride were erratic. The dihydride was consistently obtained while values obtained for the third hydrogen were consistently low, indicating that the reaction



was not going to completion. Continued hydriding at 225°C for periods up to 72 hours did not improve the values obtained. Attempts to conduct the initial hydriding at 750°C likewise proved unsuccessful. The situation was finally resolved by a hydriding-dehydriding cycling step. Typical values obtained are shown in the following table of the hydriding characteristics of crystal bar yttrium (values obtained by stepwise decomposition based on reactions (4) and (5)).

| First hydriding | | Second hydriding | |
|----------------------------|----------------------------|----------------------------|----------------------------|
| YH_2 , percent | YH_3 , percent | YH_2 , percent | YH_3 , percent |
| >90 | <80 | 100 | 101 |
| >90 | <80 | 101 | 100 |
| >90 | <80 | 94.6 | 97.6 |

Concluding Remarks

The hydriding-dehydriding technique developed for the analysis of uranium metal in urania has been successfully applied to the analysis of yttrium metal in yttria. The technique is capable of distinguishing between uranium and yttrium metal present in urania-yttria mixtures leading to a method whereby the simultaneous measurement of each is possible.

While the hydriding characteristics of yttrium metal are related to its method of preparation, the hydriding characteristics of a uranium-yttrium alloy are similar to those of the individual metal elements.

The method can be applied to the measurement of metallic uranium and/or yttrium in sintered $\text{UO}_2\text{-Y}_2\text{O}_3$ specimens subject to the following limitation; the method cannot measure uranium and/or yttrium metal that is inaccessible to hydrogen during the hydriding treatment. In general, one can expect metal deposited along a grain boundary to hydride and metal located within a grain to escape hydriding.

REFERENCES

1. Anderson, J. S., Sawyer, J. O., Warner, H. W., Willis, G. M., and Bannister M. J., *Nature* 185, (1960), 915.
2. Rothwell, E. J., *Nucl. Mat.* 6, (1962), 229.
3. Robins, R. G., *J. Nucl. Mat.* 7, (1962), 218.
4. Rothwell, E. J., *Nucl. Mat.* 5, (1962), 241.
5. Aitken, E. A., Brassfield, H. C. and McGurty, J. A., *ANS Transactions*, (1963), 153.
6. Aitken, E. A., Brassfield, H. C. and Fryxell, R. E., *Symposium on Thermodynamics with Emphasis on Nuclear Materials and Atomic Transport in Solids*, IAEA, Paper SM 66-83, Vienna, Austria, (1965).
7. Lyon, W. L., *The Measurement of Oxygen to Metal Ratio in Solid Solutions of Uranium and Plutonium Dioxides*, AEC Project Report GEAP-4271, 1963.
8. Mulford, R. N. R., Ellinger, F. H., and Zachariasen, W. H., *J. Am. Chem. Soc.* 76, (1954), 297.
9. Gueron, J., and Yaffee, L., *Nature* 160, (1947), 575.
10. Wilkinson, W. D., *Uranium Metallurgy* (Interscience Publishers, New York, 1962), Vol. 2, p. 775.
11. Hansen, M., *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), 978.
12. Hibbits, J. O., and Schaefer, E. A.; GE-TM65-9-14. (1965).
13. Flotow, H. E., Osborne, D. W., and Otto, K.; *J. Chem. Phys.* 36 (1962), 866.
14. Flotow, H. E., Osborne, D. W., Otto, K., and Abraham, B. M.; *J. Chem. Phys.* 38 (1963), 2620.

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TABLE III-I. - OXYGEN-URANIUM

RATIOS IN UO_{2-x}

| Sample number | Fuel type | Oxygen-uranium ratio | |
|---------------|-------------------|----------------------|---------------------|
| | | Oxidation technique | Hydriding technique |
| A-3 | Agglomerated ↓ | 1.883 | 1.890 |
| A-1 | | 1.913 | 1.908 |
| 85 | | 1.929 | 1.929 |
| 779-66 | | 1.938 | 1.937 |
| 779-65 | | 1.939 | 1.940 |
| A-2 | | 1.941 | 1.953 |
| 779-64 | | 1.943 | 1.938 |
| A-4 | | 1.952 | 1.954 |
| 78 | | 1.983 | 1.984 and 1.982 |
| TF-60 | | 1.988 | 1.988 |
| 890-1 | As received ↓ | 1.930 | 1.945 |
| W115 | | 1.940 | 1.971 and 1.973 |
| 894-1 | | 1.950 | 1.971 |
| 720B | | 1.987 | 1.999 |

TABLE III-II. - OXYGEN-URANIUM

RATIOS IN $W-UO_{2-x}$

| Sample number | Oxygen-uranium ratio | |
|---------------|----------------------|----------------------------------|
| | Hydriding technique | Oxidation technique ^a |
| D116-14 | 1.992 | 1.986 |
| 80 | 1.987 | 1.983 |
| 779-68 | 1.945 | 1.939 |
| D172-1 | 1.966 | 1.968 |
| D172-2 | 1.966 | 1.968 |
| D166-8 | 1.962 | 1.962 |
| D166-7 | 1.975 | 1.975 |

^aObtained on UO_2 control specimens.

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TABLE III-III. - STEPWISE DECOMPOSITION OF Th_4H_{15}

| Th, mg | Dehydriding temperature (reaction (1)), $^{\circ}\text{C}$ | H_2 recovered (reaction (1)), percent | H_2 recovered (reaction (2)), percent |
|-----------|--|--|--|
| 46.1 | 250 | 96.1 | 96.6 |
| 58.6 | 270 | 96.7 | 98.7 |
| 57.0 | 275 | 99.8 | 96.0 |
| 33.9 | 300 | 101.8 | 100.9 |
| 57.8 | 325 | 101.2 | 96.2 |
| 55.9 | 350 | 103.0 | 92.0 |
| 65.3 | 375 | 102.9 | 92.5 |
| 57.9 | 425 | 106.5 | 84.6 |

TABLE III-IV. - STEPWISE DECOMPOSITION
OF $\text{UH}_3\text{-Th}_4\text{H}_{15}$

| U, mg | Th, mg | H_2 recovered (reaction (3)), percent | H_2 recovered (reaction (4)), percent |
|----------|-----------|--|--|
| 31.8 | 33.6 | 104.5 | 105.3 |
| 39.5 | 27.6 | 99.0 | 103.7 |
| 33.3 | 27.2 | 102.2 | 98.0 |

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TABLE III-V. - ANALYSES OF 80UO₂ - 20ThO₂ SPECIMENS

(a) Starting material, as-received UO₂

| Sample | Mount number | H ₂ test conditions | | Free U, percent | Free Th, percent | Metallographic evaluation |
|--------|--------------|--------------------------------|---------------------------|-----------------|------------------|--|
| | | Time, hr | Temperature, °C | | | |
| DB-5 | C-4991 | 4 | 2400 | 4.11 | 0.04 | Uniform dispersion of small voids. The metallic phase occurs as very small particles in clusters. Difficult to determine if two phases are present because of particle size. |
| DB-6 | C-4992 | 4 | 2200 | 1.87 | .01 | Similar to DB-5 except that metallic clusters are smaller and less numerous. |
| DB-7 | C-4993 | 4 (Another portion) | 2400 (Another portion) | 2.15 2.30 | .04 .02 | Similar to DB-5. |
| DB-8 | M-7488 | 48 (Another portion) | 2400 (Another portion) | 6.64 7.07 | .06 .21 | ^a Uniform dispersion of large spherical voids throughout. A two-phase metallic precipitate has formed a continuous network throughout. |

(b) Starting material, agglomerated UO₂

| | | | | | | |
|---------------------------------------|--------|---------------------|------------------------|------------|------------|---|
| DBA-1 | C-5704 | 4 | 2400 | 3.69 | 0.11 | Uniform dispersion of large spherical voids throughout. Metallic phase occurs near the voids. |
| DBA-2 | C-5075 | 4 | 2400 | 3.80 | .10 | Similar to DBA-1. |
| DBA-3 | C-5082 | 4 (Rehydridized) | 2200 (Rehydridized) | .14 .15 | .46 .43 | ^{b, c, d} Uniform dispersion of large spherical voids throughout. A two-phase metallic precipitate at and near large voids. |
| DBA-3 (A second portion of sample) | C-5148 | 4 | 2200 | .34 | .09 | ^{b, c, d} Sample not as porous (though still very porous) as C-5082. Sample contained more free metal than observed in C-5082. |
| DBA-3 (A third portion of sample) | | 4 | 2000 | .84 | .03 | |
| DBA-4 | C-5083 | 4 | 2200 | .50 | .30 | ^{b, d} Uniform dispersion of large spherical voids throughout. Two-phase precipitate at and near the voids. |
| DBA-4 (A second portion of sample) | C-5149 | 4 | 2200 | .44 | .25 | |

^aElectron microprobe examination did not locate thorium metal in DB-8. This does not rule out the possibility that the thorium metal particles are too small to be observed.

^bElectron microprobe examination could not locate thorium metal in DBA-3 and DBA-4 mounts. The thorium metal particles may be too small to detect.

^cMetallographic examination revealed a lack of homogeneity in DBA-3.

^dElectron microprobe examination revealed that the two-phase metallic precipitate reported by metallography is metallic uranium.

TABLE III-VI. - ANALYSES OF Mo-UO₂ AND UO₂ SPECIMENS

| | ^a Mo-60UO ₂ | UO ₂ | ^a Mo-60UO ₂ | UO ₂ |
|---|-----------------------------------|-----------------|-----------------------------------|-----------------|
| Sintering time in hours, dry hydrogen at 2200° C | 4 | 4 | 16 | 16 |
| Free uranium by hydriding method | ^b 0.01 | 1.02 | ^b 0.24 | 1.72 |

^aComposition expressed as volume percent.

^bMicroprobe examination revealed that the uranium content of the Mo matrix varied from 2 to 6 weight percent with an average value of 2.5 weight percent in the 4-hour specimen and 3.5 weight percent in the 16-hour specimen. The calculated uranium content of the Mo matrix indicated 2.2 and 3.6 weight percent, respectively.

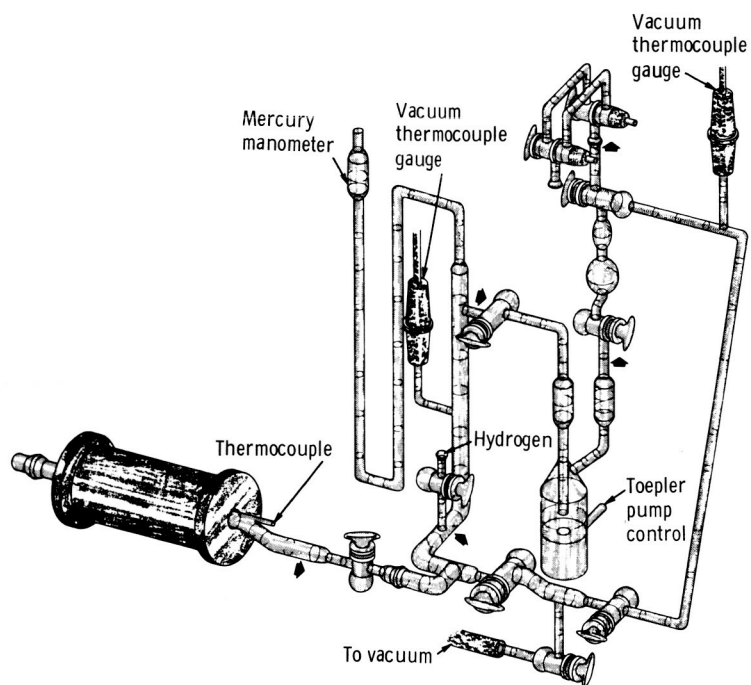


Figure III-1. - Hydriding-dehydriding apparatus.

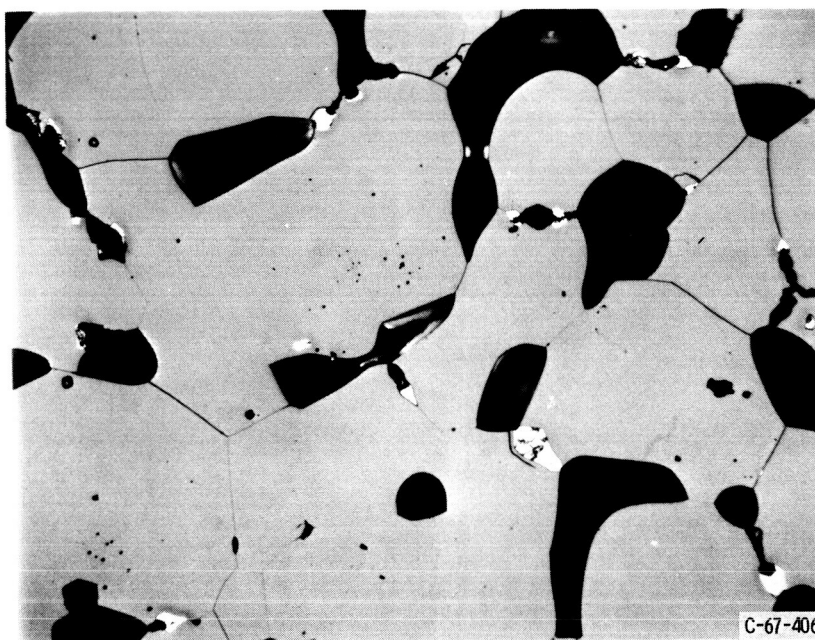


Figure III-2. - Agglomerated UO_2 ; 4 hr at 2500°C in H_2 , cooled in He (250X, etched). O/U by oxidation, 1.929; O/U by hydriding, 1.929.

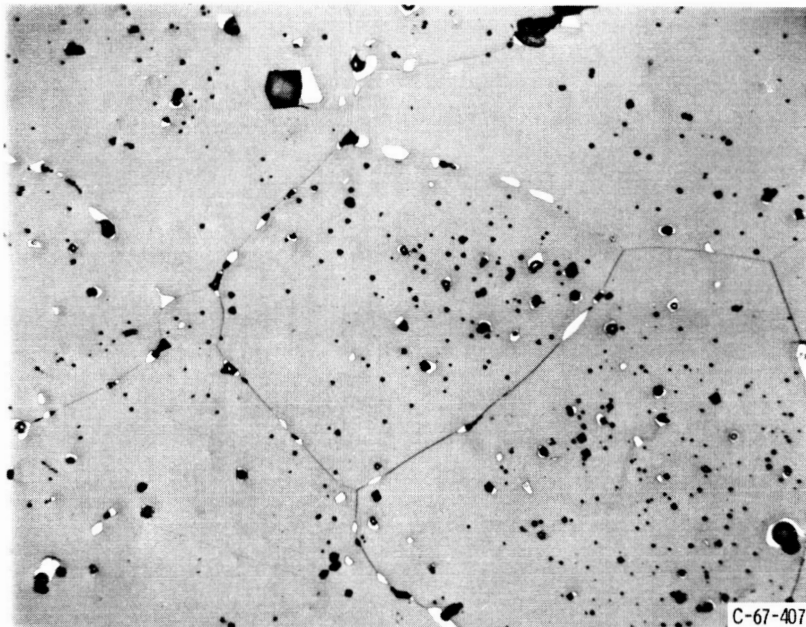


Figure III-3. - As-received UO_2 ; 6 hr at 2500°C in H_2 , cooled in He (250X, etched). O/U by oxidation, 1.930; O/U by hydriding, 1.945.

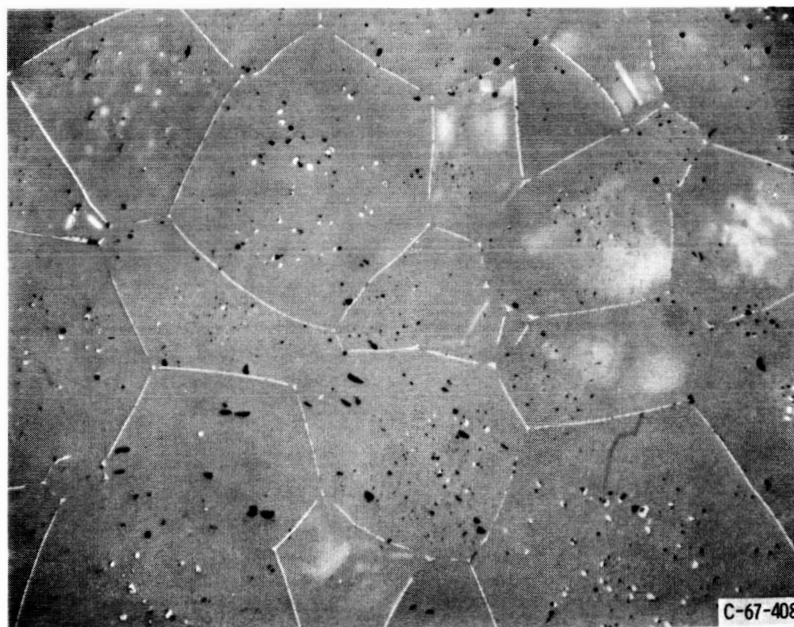


Figure III-4. - ThO_2 ; 2 hr at 1800°C in H_2 ; then 12 hr at 2600°C in H_2 ; cooled in Ar.

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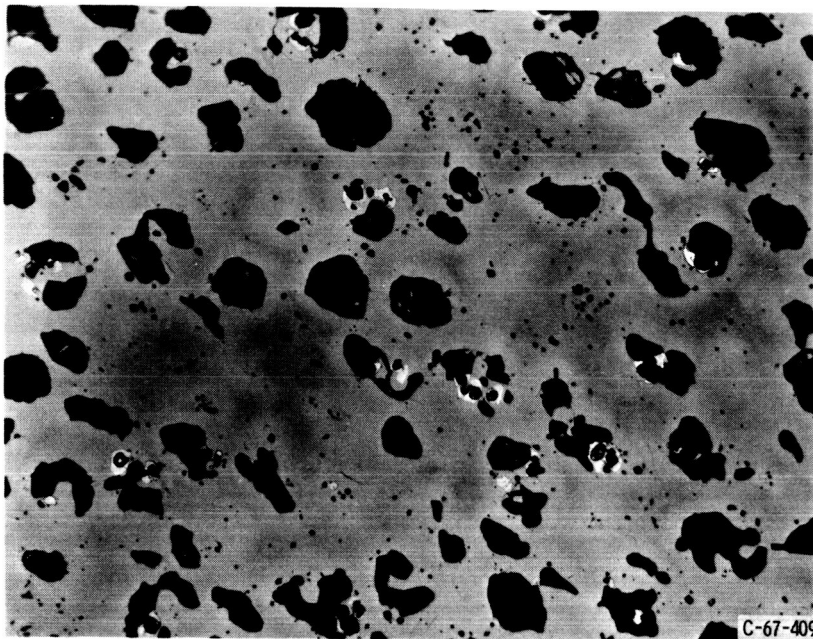


Figure III-5. - Sintered $80\text{UO}_2\text{-}20\text{ThO}_2$ (250X, as polished). Starting material, agglomerated UO_2 . (See table III-V(b), DBA-3, C-5148 for sample treatment.)

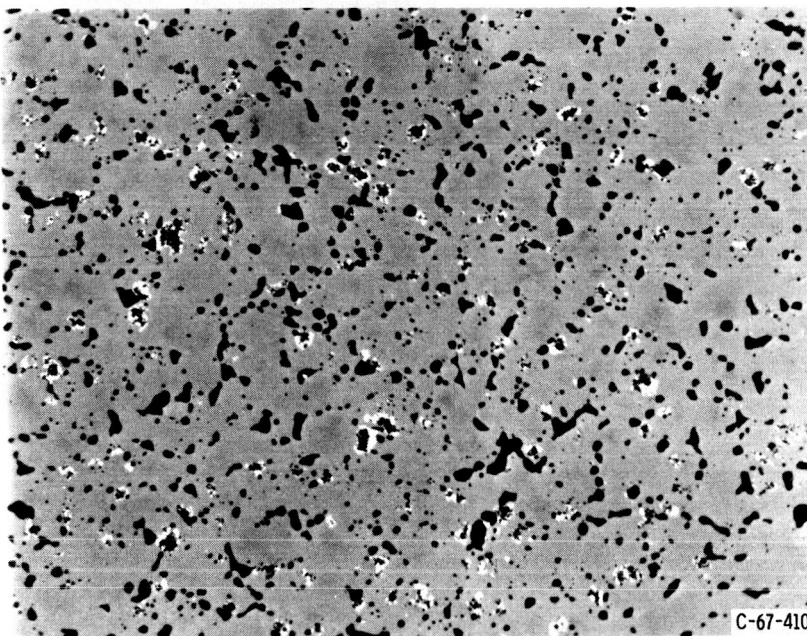


Figure III-6. - Sintered $80\text{UO}_2\text{-ThO}_2$ (250X, as polished). Starting material, as-received UO_2 . (See table III-V(a), DB-6, C-4992 for sample treatment.)

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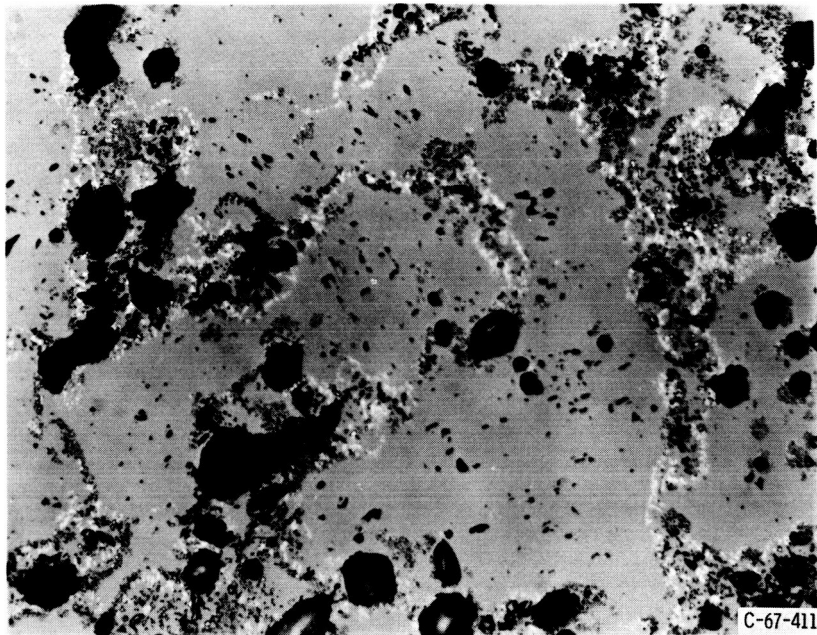


Figure III-7. - Sintered $80\text{UO}_2\text{-}20\text{ThO}_2$ (250X, as polished). Starting material, as-received UO_2 . (See table III-V(a), DB-8, M-7488 for sample treatment.)

[REDACTED]

IV. DETERMINATIONS OF OXYGEN-URANIUM RATIOS IN TUNGSTEN-URANIUM DIOXIDE PRODUCTS*

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SUMMARY

This report describes the research performed to devise a method for determining the oxygen-uranium ratio in W-UO₂ composites containing either substoichiometric, stoichiometric, or superstoichiometric UO₂. The method involves precise determinations of weight changes occurring during closely controlled oxidation and reduction processes. It is capable of obtaining precisions of ± 0.005 oxygen-uranium ratio unit.

Limited available results also are presented to indicate that this method of determining UO₂ stoichiometry can be extended to tungsten-base composites containing UO₂ with stabilizing additives in solid solution.

I. INTRODUCTION

A. Pure Uranium Oxides

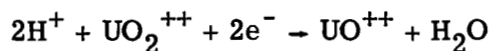
The determination of the O/U ratio is comparatively easy in samples consisting only of uranium oxide.

1. Superstoichiometry

(a) Polarography. For samples with O/U ratios between 2.00 and 2.05, the polarographic procedure is suitable for the determination of the superstoichiometry of UO₂ by reduction of UO₂⁺⁺ in a phosphoric-perchloric acid medium involving a two electron reduction (ref. 1):

* This work was performed under NASA Contract NASA 3-6209 with William A. Gordon of the NASA Lewis Research Center as the Technical Manager.

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The polarographic method is not applicable to substoichiometric UO_2 , since UO^+ and/or U^0 reduce water.

(b) Titrimetry. When the sample contains considerable UO_2^{++} , this laboratory prefers the titrimetric determination, after dissolution of the sample in phosphoric acid under a blanket of an inert gas. If preferred, the determination can be carried out coulometrically by reducing UO_2^{++} to UO^{++} .

(c) Ignition to U_3O_8 . Although this method is widely used, care must be taken that the sample does not contain any unaccounted impurities and that the composition of the ignited oxide has an O/U ratio of 2.6667 (refs. 2 and 3).

(d) Reduction of UO_2^{++} with carbon monoxide. This method (ref. 4) is rapid when a powder of small particle size is available, whereas solid material must be treated overnight to ensure complete reduction. Undoubtedly, instead of the manometric finish, the CO_2 could be measured equally well by other techniques, for example, by infrared spectroscopy or by gas chromatography. There are no data to indicate that the method is applicable to UO_2 -W mixtures.

(e) Other methods which have been used to determine the superstoichiometry of UO_2 are based on X-ray diffraction (ref. 5), quantitative metallography, the measurement of the oxygen potential using a high temperature galvanic cell (ref. 6), and the selective precipitation of UO^{++} as oxalate, fluoride, or cupferrate (ref. 7).

2. Substoichiometry

(a) It has been theorized that, when UO_2 is heated in a hydrogen-atmosphere at high temperatures, substoichiometric species, namely, UO_{2-x} , are formed which, on cooling, form $\text{UO}_{2.00}$ and U metal (ref. 8). The uranium metal thus formed can be determined by (1) conversion to uranium hydride (225°C), (2) removal of excess H_2 by evacuation to <10 microns (room temperature), (3) decomposition of UH_3 ($>350^\circ\text{C}$) and (4) gas-chromatographic measurement of the liberated hydrogen (ref. 9).

(b) The presence of metallic uranium can be verified by treating the sample with phosphoric acid in an inert atmosphere and measuring the released hydrogen after conversion to water (ref. 9).

(c) Ignition of UO_{2-x} has been used by Hibbits and Schaefer to verify their hydriding procedure (ref. 10).

B. UO_2 -W Products

Studies on the compatibility of tungsten and uranium dioxide for nuclear rocket fuel

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applications are critically dependent on accurate determinations of the O/U ratio. The sample may contain oxygen in excess of the desired O/U ratio of 2.0000. On the other hand, heating of UO_2 -W at temperatures above 2000°C in either inert or reducing atmospheres may lead to the formation of free uranium metal as a result of precipitation of the metal from a substoichiometric UO_{2-x} -phase during the cooling cycle (ref. 11).

The determination of the O/U ratio in UO_2 -W mixtures which also may contain one or more additives (Y_2O_3 , ThO_2 , CeO_2 , CaO) is considerably more difficult than the determination of the O/U ratio in pure uranium oxides. There is virtually no literature reflecting prior experience. Therefore, it was deemed advisable to evaluate a number of approaches.

2. Direct Determination of the Oxygen Content of the Sample

A direct determination of the oxygen content of the sample would represent the most desirable approach, if a sufficiently accurate procedure could be worked out. However, the effect of slight variations in the oxygen content of a sample on the O/U ratio is great, as is now demonstrated.

| O_2 , percent | U, percent | Oxygen-uranium ratio |
|---------------------------|---------------|-------------------------|
| 11.849 | 88.151 | 2.0000 |
| 11.749 | 88.251 | 1.9809 |
| 11.800 | 88.200 | 1.9907 |
| 11.839 | 88.161 | 1.9981 |
| 11.829 | 88.171 | 1.9960 |

This compilation shows that in a sample of pure UO_2 the oxygen determination would have to be accurate to ± 0.02 -percent absolute, to differentiate between an O/U ratio of 1.9950 and 2.0000. The difficulty of basing the O/U ratio on a direct determination of the oxygen content becomes even more apparent from the following example:

In the analysis of a sample consisting of 80 percent tungsten and 20 percent UO_2 ($\text{U} = 17.630$; $\text{O}_2 = 2.37$ percent), the oxygen content would have to be determined to 2.370 ± 0.0047 percent to differentiate between an O/U ratio of 1.9950 and 2.0000.

(a) Inert Gas Fusion Procedure. It was hoped that the inert gas fusion procedure could be perfected to provide oxygen results of sufficient precision. For this purpose, samples of UO_2 and U_3O_8 ranging in weight between 0.5 and 10 grams were introduced into the Leco furnace at various initial temperatures (200° to 2000°C) into baths consisting of copper, iron, or platinum. The resulting reaction product, carbon monoxide, was passed over heated copper oxide, and the CO_2 was absorbed in ascarite. The progress of the reaction was monitored by passing the gas intermittently for a few seconds into a conductometric unit connected to the assembly via a "T" connection.

Results obtained by this procedure yielded from 98.5 to 99.3 percent of the expected oxygen content and were not sufficiently precise for establishing the O/U ratio within a reasonable degree of certainty. In the case of tungsten coated UO_2 -W spheres, the oxygen recoveries ranged between 86 and 91 percent.

Additional experiments involving other fluxes and changes in equipment and manipulations did not substantially improve either the accuracy or precision.

(b) Polarographic or Coulometric Determination of UO_2^{++} . Neither approach is feasible, since solution of a UO_2 -W sample in acids leads to the reduction of hexavalent uranium compounds. The reduction, however, is not stoichiometric.

(c) Determination of Oxygen Content "By Difference". If all components of a sample, other than oxygen, could be determined with sufficient accuracy, the latter could be calculated "by difference".

A simple calculation indicates the effect of variations in U and U+W results on the O/U ratio. If oxygen is calculated "by difference", a deviation of 0.05 percent from the actual U+W content causes at the 45 percent U-level an error of 4 parts per 500 in the O/U ratio. At the 25 percent-uranium level, the same 0.05-percent deviation causes an error in the O/U ratio of 7 parts per 500.

In order to establish whether uranium-tungsten mixtures could be analyzed with sufficient accuracy to be suitable for the "Oxygen By Difference" method, various chemical procedures were investigated.

It was found that uranium and tungsten could be separated easily by ion exchange. Initially, the fusion of 5-gram mixtures, of any UO_2 -W ratio, with KHSO_4 in quartz crucibles was successfully carried out. The melt leached in an appropriate HF-HCl mixture, and the two components, uranium and tungsten, were quantitatively separated by anion exchange. Further extension of the tests produced the following simplified procedure:

Five grams of the UO_2 -W sample are heated in a 400 ml Teflon beaker with concentric nitric acid (platinum dishes or beakers cannot be used. Since in the subsequent acid treatment hydrated tungstic oxides form which adhere to platinum and do not dissolve in hydrofluoric acid). HF is added to the warm solution, and, if required, more HNO_3 is added until the sample is completely decomposed. The solution is evaporated to dryness on a steam bath and treated several times with HNO_3 to oxidize and dissolve any UF_4 and UO_2 .

The hydrated tungstic oxide is dissolved by several treatments with HF, with intermittent evaporations to dryness. When the salts finally can be dissolved in less than 5 ml of hydrofluoric acid, 25 ml of HF, 95 ml of H_2O , and 175 ml of HCl are added in succession.

The clear solution is passed through 15 inches (1 in. o.d.) of 100 to 200 mesh Dowex-1 (8x) anion exchange resin, and the tungsten is subsequently eluted with

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600 ml of a mixture of 60 to 10 to 30 HCl, HF, and H₂O. After the elution of the tungsten, the uranium is eluted with 700 ml of 2N HNO₃.

The tungsten is determined by evaporation of the HCl-HF solution, first in a Teflon beaker, then in the presence of H₂SO₄ in a platinum dish. After ignition at 750° C, it is finally weighed as WO₃.

The uranium is determined after evaporation of the nitric acid solution to fumes with H₂SO₄. After repeated evaporations, with the intermittent addition of H₂O, the sulfuric acid solution is passed, without aliquoting, through a Jones reductor. After aeration, the UO⁺⁺ is oxidized, first by adding an aqueous solution of a weighed amount of K₂Cr₂O₇, then by titrating the small amount of unoxidized uranium with a weak solution of K₂Cr₂O₇.

The above procedure must be modified to remove or compensate for the effect of other elements in the sample present, either as contaminations or as additives.

The tungsten can also be determined by precipitation with 8-hydroxyquinoline. The quinolate is a very attractive weighing form.

The uranium can also be determined by evaporation of the eluate and conversion to U₃O₈.

Some of the results obtained in separating and determining uranium and tungsten as described above are presented in table IV-I.

TABLE IV-I. - DETERMINATION OF "OXYGEN BY DIFFERENCE" AND
SEPARATION OF URANIUM AND TUNGSTEN BY ION EXCHANGE

[Expected O-U ratio, 2.0000.]

| Analysis number | Tungsten taken, g | Uranium dioxide taken, g | Uranium equivalent, g | Tungsten found, g | Uranium found, g | Oxygen by difference, g | Oxygen-uranium ratio |
|-----------------|-------------------|--------------------------|-----------------------|-------------------|------------------|-------------------------|----------------------|
| 1 | 3.0000 | 2.0000 | 1.7630 | 3.0009 | 1.7638 | 0.2353 | 1.9849 |
| 2 | 3.0000 | 2.0000 | 1.7630 | 3.0015 | 1.7635 | .2350 | 1.9828 |
| 3 | 4.0000 | 1.0000 | .8815 | 4.0018 | .8821 | .1161 | 1.9583 |
| 4 | 4.0000 | 1.0000 | .8815 | 4.0009 | .8812 | .1179 | 1.9908 |
| 5 | 3.5000 | 1.5000 | 1.3223 | 3.4987 | 1.3219 | .1794 | 2.0194 |
| 6 | 3.5000 | 1.5000 | 1.3223 | 3.5007 | 1.3229 | .1764 | 1.9841 |

The data in table IV-I clearly indicate that an accurate determination of the O/U ratio (ability to differentiate between 1.9950 and 2.0000) is not feasible by the "oxygen by difference" method, even though the determination of both uranium and tungsten can be achieved with a remarkable degree of accuracy. For instance, at the 20-percent UO₂ level, an error of approximately 1 part per 8000 in the UO₂+W determination causes an

approximately 1 part per 200 error in the O/U ratio (analysis number 4 of table IV-I).

Although the determination of the O/U ratio by the oxygen by difference method appears to be impractical, uranium results obtained by the ion exchange approach are more adequate for the calculation of the O/U ratio by the " ΔO_2 Method" described in section II-A-2.

2. Deviation From Stoichiometry Method (ΔO_2 Method)

Since neither the direct oxygen determination nor the indirect by difference approach yields data sufficiently reliable to allow the division of an oxygen result by an uranium result, efforts were made to measure the O/U ratio by determining the deviation from stoichiometry.

The hydriding procedure developed by Hibbits (ref. 10) is an excellent example of this type of approach. Measurement of free uranium provides a direct measurement of the deviation from stoichiometry in substoichiometric UO_2 , if the underlying assumption that such UO_x consists of free uranium and UO_2 is correct. This method, of course, is not applicable to superstoichiometric UO_2 . On the other hand, the familiar polarographic determination of UO_2^{++} in a phosphoric acid solution of UO_2^{++} provides such a direct measurement of superstoichiometric deviations. Unfortunately, as was pointed out before, this method is not applicable to W- UO_2 composites, as the tungsten reduces part or all of the UO_2^{++} .

One of the commonly used methods for determining the stoichiometry of pure uranium oxides consists in heating samples in air at $850^\circ C$ and weighing the resulting U_3O_8 . Calculating back to UO_2 , any deviation from stoichiometry is revealed as a difference between the original sample weight and the calculated UO_2 weight. In the presence of tungsten, such a procedure would, of course, be complicated by simultaneous oxidation of tungsten to WO_3 . Experiments carried out along these lines, which are described in section III-A, indicate that the oxidation is further complicated by the partial formation of uranyl tungstate (UO_2WO_4) at temperatures depending on the U/W ratio. (However, conditions further discussed in section III-A have been established to assure a consistent oxidation of UO_2 -W mixtures to U_3O_8 plus WO_3 . Since the relative gain in weight of UO_2 on oxidation to U_3O_8 is only 3.95, whereas tungsten gains 26.09 on oxidation to WO_3 , the gain in weight represents a simple way to calculate the relative proportions of the two components.)

Although the change in weight on oxidation cannot be directly used for the calculation of the O/U ratio, the oxidized product was found to be readily reduced by hydrogen at $900^\circ C$ to stoichiometric UO_2 and metallic W. In the case of large samples of UO_2 -W or samples coated with tungsten, it is necessary to partially oxidize the sample only to the

extent that the hydrogen can penetrate the entire structure of the sample during the reducing cycle.

Comparison of the weight of the reduced product with the original sample weight provides therefore a direct measurement of the excess or deficiency of oxygen in the original material. If the weight of the reduced product is less than the starting weight, then the sample has an O/U ratio indicating superstoichiometry. If the weight of the reduced product is greater than the starting weight, then the sample has an O/U ratio indicating substoichiometry.

II. EXPERIMENTAL

A. Procedure

1. Determination of Tungsten and UO_x by "Gain Method"

Weighed amounts of tungsten powder (hydrogen reduced prior to use or of known oxygen content) and $\text{UO}_{2.0000}$ powder are weighed into 25-ml platinum crucibles. The powders are mixed, then ignited, first at about 500°C , then gradually to 600° to 700°C as further discussed in section III-A. The crucibles are held at the upper temperature for 4 hours, then are cooled in a desiccator and weighed.

The percentage of UO_x and tungsten are derived from the following formulas.

$$\text{Percent } \text{UO}_2 = 117.84 - (4.5167 \times \text{percent gain in weight})$$

$$\text{Percent W} = (4.5167 \times \text{percent gain in weight}) - 17.84$$

2. Determination of Sub- and Superstoichiometry of UO_2 in $\text{UO}_2\text{-W}$

(a) Hydrogen Reduction Method. The platinum crucible containing the oxidized product ($\text{U}_3\text{O}_8 + \text{WO}_3$) is placed into a slightly larger clay (or porcelain) crucible. The platinum crucible is covered with a perforated platinum sheet, which serves to disperse the argon and/or hydrogen introduced through a clay tube extending just inside the clay crucible. To carry out the reduction, air is replaced by argon (about 200 ml/min). After approximately 5 minutes, the argon is substituted by a flow of approximately 200 ml per minute of hydrogen. The crucible is heated to about 900°C , held at this temperature for about 1 hour, cooled to about 500°C in hydrogen, and then cooled to room temperature in argon. As discussed below, the weight of the $\text{UO}_2 + \text{W}$ determines whether the O/U ratio of the

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original sample is stoichiometric, substoichiometric, or superstoichiometric.

The O/U ratio of the sample is calculated by the following formula:

$$X = 2 - \frac{2\Delta}{\text{wt } \text{UO}_2 \times 0.11849}$$

where

Δ deficiency of oxygen compared to O/U = 2.0000

$-\Delta$ excess of oxygen compared to O/U = 2.0000

(b) Hydriding Procedure. A small platinum boat containing an appropriate amount of sample is placed into a 1-inch-diameter Vycor combustion tube. The system is evacuated, flushed with hydrogen, and reevacuated to below 10 microns. Hydrogen is then admitted to provide about 1 atmosphere of pressure and the system is sealed. The sample is then heated to 225° C and the temperature maintained for 4 to 5 hours. The sample is cooled to room temperature and the excess hydrogen removed by evacuation. The system is then sealed again and heated to 600° C. The released hydrogen is transferred via a Toepler pump to a gas collecting bulb. An aliquot is then analyzed chromatographically. Unless the purity of the hydrogen is in question, a manometric measurement of the total released gas is more rapid and, in the case of O/U ratios below 1.9, probably more accurate than the gas chromatographic measurement.

The O/U ratio of the sample is calculated as follows:

$$\text{O/U ratio} = 2 - \Delta$$

$$\Delta = \frac{2 \times \text{Metallic U}}{\text{Total U}}$$

$$\text{Metallic U} = 79.356 \times \text{H}_2$$

III. RESULTS AND DISCUSSION

A. Gain Method

The formulas used in section II-A-1 are based on the following considerations:

$$\text{Factor } \text{UO}_2 \rightarrow \text{U}_3\text{O}_8 = 1.0395$$

$$\text{Factor W} \rightarrow \text{WO}_3 = 1.2609$$

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$$\text{Percent UO}_2 = x$$

$$\text{Percent W} = 100 - x$$

Then

$$(1.0395x - x) + 1.2609(100 - x) - (100 - x) = \text{Gain in percent}$$

Solving the above for x (UO_2) yields

$$\text{Percent UO}_2 = 117.84 - 4.5167 \text{ percent gain} \quad (1)$$

Solving the above for $100 - x$ (W) yields

$$\text{Percent W} = 4.5167 \text{ percent gain} - 17.84 \quad (2)$$

The following example illustrates the calculations in terms of percentage weight gains upon oxidation:

Given sample composition:

$$\text{UO}_2 (10 \text{ percent}) + \text{W} (90 \text{ percent})$$

Percent of original sample weight upon oxidation:

$$\text{U}_3\text{O}_8 (10.395 \text{ percent}) + \text{WO}_3 (113.481 \text{ percent})$$

Total percent gain:

$$0.395 + 23.481 = 23.876$$

Percent UO_2 (from eq. (1)):

$$117.84 - (4.5167 \times 23.876) = 10$$

Percent W (from eq. (2)):

$$(4.5167 \times 23.876) - 17.84 = 90$$

Further illustration is provided by the results of two determinations involving two different W- UO_2 mixtures recorded in table IV-II.

TABLE IV-II. - OXIDATION OF $\text{UO}_2 + \text{W}$ to $\text{U}_3\text{O}_8 + \text{WO}_3$

| | Test 1 | Test 2 |
|---|--------|--------|
| Tungsten taken, g | 2.9910 | 4.9850 |
| UO_2 taken, g | 3.0000 | 1.0003 |
| UO_2 taken, percent | 50.08 | 16.71 |
| Expected gain from $\text{W} \rightarrow \text{WO}_3$, g | .7804 | 1.3006 |
| Expected gain from $\text{UO}_2 \rightarrow \text{U}_3\text{O}_8$, g | .1185 | .0395 |
| Total expected gain, g | .8989 | 1.3401 |
| Actual gain, g | .9079 | 1.3400 |
| Actual gain, percent | 15.154 | 22.390 |
| UO_2 calculated, percent | 49.39 | 16.71 |

In the case of test 2, the UO_2 results obtained by the Gain method (see table IV-2) agree well with the UO_2 taken for the analysis. In the case of test 1, the UO_2 result is approximately 0.70 percent on the low side. The low result is due to 9 mg in excess of the expected gain resulting from the oxidation of W and UO_2 . How can this excessive oxidation of 9 mg be explained, particularly in view of the fact that a specific W- UO_2 ratio will always produce excessive oxidation above a specific temperature?

Trumov, et al. (ref. 11) have shown that double oxides of uranium with tungsten are formed by cocalcining of their oxides in air at temperatures of 800° to 1000° C. When stoichiometric amounts of uranium and tungsten oxides are heated at 900° C in air, UO_2WO_4 is formed. When an excess of tungstic oxide is present, the end-product is $\text{UO}_2\text{WO}_4 + \text{WO}_3$. The formation of UO_2WO_4 has been confirmed by Juenke and Bartram (ref. 12).

It is rather easy to conjecture a mechanism for the fact that uranium is oxidized to a valence state beyond U_3O_8 . Since U_3O_8 consists of UO_3 - UO_3 - UO_2 , the UO_3 part probably reacts with WO_3 to form UO_2WO_4 . This leads to the formation of free UO_2 which in turn is oxidized to U_3O_8 which then will react with additional WO_3 . This process of oxidation and uranyl tungstate formation conceivably continues, if there is intimate contact between the uranium and tungsten oxide, until all the uranium is oxidized to UO_3 . This is difficult in practice, unless the two oxides are mixed prior to calcining as was done by references 12 and 11.

In the case of UO_2 -W powders, plates, or spheres, the formation of UO_2WO_4 is not only temperature-dependent, but is also dependent on the UO_2/W ratio. In the case of high W concentrations ($\text{W}/\text{UO}_2 = 5$ to 1), complete oxidation can only be obtained at 700° C, while in the case of a 1 to 1 mixture of W- UO_2 , oxidation is already complete at 600° C.

It is not difficult to conjecture a mechanism for the fact that high W concentrations lead to complete oxidation only at 700° C, while the oxidation of high UO_2 concentrations is already complete at 600° C. In the absence of UO_2 , oxidation of W to WO_3 is rapid at 650° C. On the other hand, oxidation of UO_2 is comparatively slow at this temperature. The oxidation of W to WO_3 leads to an approximately tenfold increase of volume, while the oxidation of UO_2 to U_3O_8 does not increase the volume to any significant extent. When a mixture of UO_2 and W is ignited, the UO_2 is therefore surrounded - with an increase in the W/UO_2 ratio - by increasing layers of WO_3 , thus limiting the access or impeding the transfer of oxygen. Consequently, in the presence of excess tungsten, the temperature must be raised to achieve complete oxidation of UO_2 . It was, however, noticed that the WO_3 catalytically oxidizes the uranium oxide, or acts as a transfer agent to the extent that it is never necessary to heat the mixture above 700° C, which is far below the usually recommended temperature for the conversion of UO_2 to U_3O_8 . Results of the ignition study are presented in table IV-III.

TABLE IV-III. - EFFECT OF TEMPERATURE
ON THE GAIN METHOD

| | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 |
|---|--------|--------|--------|--------|--------|
| W taken, g | 3.9880 | 2.9910 | 3.0181 | 4.9850 | 2.4925 |
| UO ₂ taken, g | 2.0000 | 3.0000 | 2.0000 | 1.0000 | 3.5000 |
| U ₃ O ₈ taken, g | ----- | ----- | .0933 | ----- | ----- |
| Total expected gain, g | 1.1195 | .8989 | .8664 | 1.3401 | .7886 |
| Gain - 3 hr at 500° C | 1.1097 | .8910 | .8630 | 1.3280 | .7822 |
| Gain - 5 hr at 550° C | 1.1135 | .8960 | .8650 | 1.3335 | .7865 |
| Gain - 3 hr at 600° C | 1.1194 | .8994 | .8668 | 1.3365 | .7880 |
| Gain - 3 hr at 650° C | 1.1205 | .9034 | .8690 | 1.3385 | .7986 |
| Gain - 3 hr at 700° C | 1.1215 | .9064 | .8700 | 1.3404 | .8020 |
| Identical W/U mixtures after heating 1 hr at 500° C | | | | | |
| 2 hr at 600° C | 1.1190 | 0.8990 | 0.8660 | 1.3370 | 0.7880 |
| 1 hr at 700° C | 1.1230 | .9057 | .8705 | 1.3407 | .8050 |

It should be pointed out that the tests described in table IV-III were repeated a number of times, both in platinum crucibles of various sizes and in platinum boats, in order to ensure that the rate of oxidation is not dependent on the geometry of the platinum vessel.

It also should be mentioned that the method only provides a total uranium figure calculated to UO₂. If the sample is super- or substoichiometric, the true O/U ratio can be determined only by a simultaneous determination of ΔO_2 (excess or deficiency of oxygen) by one of the methods described below.

Oxidation of sintered UO₂-W compacts may require some modification of the oxidation procedure described above. Whereas sintered UO₂-W (~1 to 1) pieces, with O/U ratios of < 2.0, were found to oxidize readily, particles coated with tungsten or fuel

plates may require heating in air, in a muffle furnace, at temperatures up to 700° C, irrespective of the UO₂-W content. In such cases, also when samples of unknown compositions are analyzed, it is recommended that the oxidation be started at about 500° C and concluded at 700° C. After cooling in a desiccator, the oxides are weighed and the approximate UO₂ and W content determined by the formula previously described. The platinum crucible is then placed inside a porcelain Rose crucible and heated in a stream of hydrogen at 900° C to determine ΔO₂ as described in section II-B. Subsequently, the UO₂-W mixture (not a compact as the original sample, now a nondense powder) is heated in a muffle furnace at the temperature appropriate for the particular composition (see table IV-III). The reduction and oxidation steps can be repeated, if there exists any doubt as to their completeness.

B. ΔO₂ PROCEDURES

1. Hydrogen Reduction Method - The formula used in section II-A-2 involves the following terms:

| | |
|--------------------------|---|
| wt UO _x | weight of uranium oxide in sample |
| wt W | weight of tungsten in sample |
| wt UO ₂ | weight of UO ₂ in reduced sample |
| wt UO _x +wt W | wt S = weight of sample |
| wt UO ₂ +wt W | wt R = weight of reduced sample |
| X | O/U ratio |
| Δ | deficiency of oxygen compared to O/U = 2.0000 |

The stoichiometry then is calculated as follows:

$$\frac{\Delta}{\text{wt O}_2} = \frac{2-X}{2}$$

$$\text{wt O}_2 = \text{wt UO}_2 \times 0.11849$$

Then,

$$\frac{2\Delta}{\text{wt UO}_2 \times 0.11849} = 2-X$$

$$X = 2 - \frac{2\Delta}{\text{wt UO}_2 \times 0.11849}$$

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Example:

A 5-gram sample of a UO_2 -W compact is oxidized at 700°C , then weighed, reduced in hydrogen, and weighed again.

The gain in weight is 1.1703 g

$$\text{wt R} = 4.9890 \text{ g}$$

$$- \Delta = 0.0110 \text{ g}$$

Gain in weight (based on the reduced sample) is

$$\begin{array}{r} 1.1703 \text{ g} \\ (5) \quad \underline{.0110 \text{ g}} \\ 1.1813 \text{ g} = 23.678 \text{ percent} \end{array}$$

$$\text{UO}_2 = 117.84 - (4.5167 \times 23.678) \text{ (See section II-A-1)}$$

$$\text{UO}_2 = 0.5433 \text{ g}$$

$$X (\text{O/U ratio}) = 2 + \frac{2 \times 0.0110}{0.5433 \times 0.11849}$$

$$X = 2 + 0.3417$$

$$\text{O/U ratio} = 2.3417$$

Alternate Way of Calculating the O/U Ratio:

$$0.5433 \text{ g UO}_2 = 0.47892 \text{ g U} + 0.06438 \text{ g O}_2$$

$$\begin{array}{r} \text{Total U} = 0.47892 \text{ g; Total O}_2 = .06438 \text{ g (UO}_2) \\ + \underline{.0110 \text{ g (- } \Delta)} \\ 0.07538 \text{ g} \end{array}$$

$$\text{O/U ratio} = \frac{0.7538}{16.00} \times \frac{238.07}{0.47892} = 2.3419$$

The reduction procedure described in section II-A-2 and just discussed further is valid for any mixture of tungsten with either substoichiometric or superstoichiometric UO_2 . The reduction can be affected by the presence of various additives, such as

Y_2O_3 , CaO, ThO_2 , and CeO_2 . Experiments carried out up to this time have established the following results:

(a) When a sample of superstoichiometric UO_2 -W containing CaO was ignited in air, the presence of CaO had no effect on the oxidation characteristics of the mixture. When the oxidized fraction was reduced at $900^\circ C$ in hydrogen, the following data were obtained:

| | Type of sample | | | |
|---------------------|----------------|---------------|------------------------------|-------------------------------|
| | 5 g W- UO_2 | 5 g W- UO_2 | 5 g W- UO_2 + 50 mg CaO | 5 g W- UO_2 + 100 mg CaO |
| Expected gain, g | 1.1680 | 1.1680 | 1.1680 | 1.1680 |
| Actual gain, g | 1.1675 | 1.1690 | 1.1695 | 1.1675 |
| Expected - Δ | .0110 | .0110 | .0110 | .0110 |
| Actual - Δ | .0108 | .0111 | -.0434 | -.0280 |

In other words, at a temperature of $900^\circ C$, it is impossible to reduce quantitatively the U_3O_8 - WO_3 -CaO mixture. This indicates that the CaO combines with either the uranium or the tungsten oxide to form a stable product. An examination of the ignited mixture under an ultra-violet light source revealed the presence of $CaWO_4$.

(b) It was found that CeO_2 does not affect the reduction of the U_3O_8 - WO_3 mixture.

(c) When the effect of Y_2O_3 was investigated, it was noted that the Y_2O_3 did not affect the oxidation characteristics of the UO_2 -W mixture. Unfortunately, as in the case of CaO, attempts to reduce quantitatively the oxidized product with hydrogen at $900^\circ C$ failed. It was noted, however, that reduction of Y_2O_3 was considerably more complete than in the case of CaO. Further tests established the fact that reduction is complete at about $1100^\circ C$.

(d) The reduction with hydrogen at $1100^\circ C$ is difficult with a Rose crucible type arrangement. Hence, platinum boats were used for both the oxidation and reduction steps. The reduction was carried out in a quartz combustion tube heated to $1100^\circ C$ in a Tube furnace.

(e) Since the reduced tungsten metal markedly attacks the platinum at $1100^\circ C$, other boats were investigated. Nickel boats were found to be extraordinarily suited for the reduction step. It was found that nickel boats preignited in air at 500° to $600^\circ C$, then reduced in hydrogen, and cooled in argon, will maintain a constant weight, irrespective of how often the oxidation and reduction cycles are repeated. Nickel boats are fabricated from nickel sheet. Although they are also attacked at $1100^\circ C$ by tungsten metal, the attack is much less severe than in the case of platinum. Furthermore, the nickel boats are so inexpensive that they can be discarded after one use.

(f) When nickel boats are used, the oxidation step is carried out in a platinum crucible. The reduction step in nickel preferably is carried out on a separate portion of the

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sample and requires only partial oxidation of the $\text{UO}_2\text{-W}$. When the amount of sample is limited or where homogeneity considerations dictate that the total sample be consumed, the weighed oxidized product can be transferred to a tared preignited (air, then H_2) nickel boat and reweighed prior to reduction.

(g) The nickel boats used are 15 cm long and 18 mm high. They are capable of handling 10 grams or more of sample, thus allowing a more precise determination of the ΔO_2 .

2. Hydriding Procedure - The formula for calculating the O/U ratio was previously given as

$$\Delta = \frac{2 \times \text{Metallic U}}{\text{Total U}}$$

The following example illustrates the calculation mechanism:

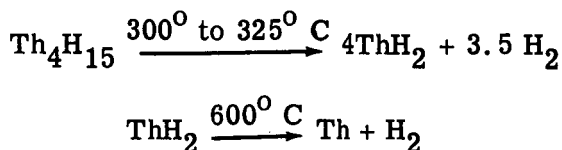
1 g sample yields 43 and 41 μg of H_2

$$79.356 \times 42 = 3333 \mu\text{g U} = 0.333 \text{ percent U metal}$$

$$\Delta = \frac{2 \times 0.333}{88.19} = 0.00755$$

$$2 - \Delta = 2 - 0.00755 = 1.9925$$

It has been shown that thorium can be hydrided at 225°C and dehydrided at 600°C using the same conditions described for uranium. The composition of the hydride is Th_4H_{15} . The evolution of hydrogen in the dehydriding step appears to proceed stepwise. Hibbits and Schaefer (ref. 10) have reported the following sequence.



The simultaneous determination of metallic uranium and metallic thorium should be possible merely by lowering the dehydriding temperature for uranium from 600° to 325°C .

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IV. EFFECT OF ERRORS IN THE ΔO_2 AND UO_2 DETERMINATION ON THE O/U RATIO

It was shown that the UO_2 content of a sample can be determined with a high degree of precision by a chemical (ion exchange) procedure and with a somewhat lesser degree of precision by a physical (gain method) procedure. ΔO_2 is determined separately by either the hydrogen reduction or hydriding procedures. In table IV-IV an attempt is made to determine the effect of possible errors in the determination of UO_2 and/or ΔO_2 on the determination of the O/U ratio.

TABLE IV-IV. - EFFECT OF VARIATIONS IN ΔO_2
AND/OR UO_2 DETERMINATIONS ON O/U RATIO

| Example | UO_2 found, percent | $-\Delta O_2$ found, percent | Total U, percent | Total O_2 , percent | O/U ratio |
|---------|-----------------------------|------------------------------------|------------------------|-----------------------------|-----------|
| 1 | 11.80 | 0.22 | 10.402 | 1.618 | 2.3143 |
| 2 | 11.80 | .21 | 10.402 | 1.608 | 2.3001 |
| 3 | 11.90 | .22 | 10.490 | 1.630 | 2.3120 |
| 4 | 25.00 | .22 | 22.038 | 3.182 | 2.1483 |
| 5 | 25.00 | .21 | 22.038 | 3.172 | 2.1416 |
| 6 | 25.10 | .22 | 22.126 | 3.194 | 2.1479 |
| 7 | 25.50 | .22 | 22.479 | 3.241 | 2.1453 |
| 8 | 45.00 | .22 | 39.668 | 5.552 | 2.0825 |
| 9 | 45.00 | .21 | 39.668 | 5.542 | 2.0788 |
| 10 | 45.50 | .22 | 40.109 | 5.611 | 2.0815 |
| 11 | 45.50 | $+\Delta .22$ | 40.109 | 5.171 | 1.9185 |

The data in table IV-IV allow several conclusions:

1. A 0.1 percent error in the UO_2 determination has very little effect on the O/U ratio. At the 12-percent UO_2 level, the error is 1 part per 1000 (example 3), and at the 25-percent UO_2 level, 1 part in 5000 (example 6). A 0.5 percent error in the UO_2 determination affects the O/U ratio at the 25-percent UO_2 level to the extent of 1 part in 700 (example 7), and at the 50-percent UO_2 level, 1 part in 2000. These examples demonstrate that an accurate determination of the O/U ratio does not require an accurate UO_2 figure. The gain method described earlier, if carried out with a 5-gram sample weight, is more than adequate for this purpose.

2. As would be expected, the ΔO_2 determination is extremely critical. At the 12-, 25-, and 45-percent UO_2 level, a 0.01-percent error in the ΔO_2 determination causes errors of 1 part in 160, 1 part in 300, and 1 part in 600, respectively. It must therefore be emphasized that it is necessary for an accurate determination of the U/O ratio to

use in the reduction step a sample weight adequate to yield ΔO_2 results with a precision greater than 0.01 percent.

3. The calculation of the O/U ratio by the hydriding procedure (see section II-A-2-b) indicates that a 10-percent error in the U-metal determination ($U = 0.33$ percent, $UO_2 = 25$ percent) causes an error of only about 1.5 parts per 1000. Since the accuracy of the U metal determination is substantially better than 10 percent (provided an optimum sample weight is taken for the analysis), the hydriding procedure, when applicable, represents a superior method for determining the substoichiometry of a sample.

V. VERIFICATION OF PROPOSED PROCEDURES

A. SUPERSTOICHIOMETRY

Five-gram portions of superstoichiometric UO_2 received from NASA were ignited to U_3O_8 in air at $850^\circ C$. The increase in weight (5.0007 g UO_x to 5.1560 g U_3O_8) signifies an O/U ratio of 2.1383.

Tests carried out with this superstoichiometric UO_2 are described:

| | | |
|---------------------------------|----------------------------------|----------------------------------|
| W taken, g | 5.0000 | 4.0000 |
| UO_x taken, g | 1.0000 | 2.0000 |
| Gain, g | 1.3368 | 1.1105 |
| $-\Delta O_2$, g | 0.0081 | 0.0162 |
| Gain in reduced sample, g | 1.3449 | 1.1267 |
| Gain in reduced sample, percent | $\frac{1.3449}{5.9919} = 22.445$ | $\frac{1.1267}{5.9838} = 18.829$ |

Calculation:

$$\begin{aligned}
 UO_2 &= 117.841 - (4.5167 \times 22.445) \\
 UO_2 &= 16.464 \text{ percent} \\
 \times 0.88151 &= 14.513 \text{ percent U} \\
 16.464 - 14.513 &= 1.95 \text{ percent } O_2 \text{ in } UO_2 \\
 &\quad + 0.135 \text{ percent } \Delta O_2 \\
 &\quad 2.085 \text{ percent total } O_2
 \end{aligned}$$

$$O/U \text{ ratio } \frac{2.085 \times 238.07}{14.513 \times 16} = 2.1376$$

$$\text{Actual} = 2.1383$$

$$\begin{aligned}
 UO_2 &= 117.841 - (4.5167 \times 18.829) \\
 UO_2 &= 32.796 \text{ percent} \\
 \times 0.88151 &= 28.910 \text{ percent U} \\
 32.796 - 28.910 &= 3.886 \text{ percent } O_2 \text{ in } UO_2 \\
 &\quad + 0.270 \text{ percent } \Delta O_2 \\
 &\quad 4.156 \text{ percent total } O_2
 \end{aligned}$$

$$\frac{4.156 \times 238.07}{28.910 \times 16} = 2.1390$$

$$\text{Actual} = 2.1383$$

B. SUBSTOICHIOMETRY

Five-gram portions of substoichiometric UO_2 received from NASA were ignited to U_3O_8 in air at 850°C . The increase in weight (5.0002 g UO_x to 5.1999 g U_3O_8) signifies an O/U ratio of 1.9928.

The substoichiometry was checked by the hydriding procedure. The 1-gram sample yielded 42 μg of H_2 equivalent to 0.33 percent U.

According to: $\frac{\text{Metallic U}}{\text{Total U}} = \frac{\Delta}{2.0000}$, the substoichiometry would be 1.9926.

Tests carried out with this substoichiometric UO_2 are described:

| | | |
|---------------------------------|----------------------------------|----------------------------------|
| W taken, g | 5.0000 | 4.0000 |
| UO_x taken, g | 1.0000 | 2.0000 |
| Gain, g | 1.3460 | 1.1210 |
| ΔO_2 , g | 0.0008 | 0.0012 |
| Gain in reduced sample, g | 1.3452 | 1.1198 |
| Gain in reduced sample, percent | $\frac{1.3452}{6.0008} = 22.417$ | $\frac{1.1198}{6.0012} = 18.660$ |

Calculation:

| | |
|---|---|
| $\text{UO}_2 = 117.841 - (4.5167 \times 22.417)$ | $\text{UO}_2 = 117.841 - (4.5167 \times 18.66)$ |
| $\text{UO}_2 = 16.590$ percent | $\text{UO}_2 = 33.560$ percent |
| $\times 0.8815 = 14.624$ percent U | $\times 0.88151 = 29.583$ percent U |
| $16.590 - 14.624 = 1.966$ percent O_2 in UO_2 | $33.560 - 29.583 = 3.977$ percent O_2 in UO_2 |
| $- .013$ percent ΔO_2 | $- .020$ percent ΔO_2 |
| 1.953 percent total O_2 | 3.957 percent total O_2 |
| O/U ratio $\frac{1.953 \times 238.07}{14.624 \times 16} = 1.9871$ | O/U ratio $\frac{3.957 \times 238.07}{29.583 \times 16} = 1.9903$ |
| Actual 1.9926 | Actual 1.9926 |

REFERENCES

1. Kubota, H., Anal. Chem.; 32, 611 (1960).
2. Payne, E. C., U. S. Atom. Energy Comm., NBL-156 (1959).
3. Stonhill, L. G., Can. J. Chem.; 37, 454 (1959).
4. Marken, T. L., Walter, A. J., and Bones R. J., AERE Report R 4608 (1964).

~~CONFIDENTIAL~~

5. Bensey, F. N. and Eckert, A. C., U. S. Atom. Energy Comm. AECD-2581 (1949).
6. Marken, T. L., and Bones, R. J., U.K.A.E.A. Report, AERE-R 4042.
7. Booman, G. L., and Rein, J. E., in Kolthoff and Elving's "Analytical Treatise", Part II, Vol. 9.
8. Hibbits, J. O., and Schaefer, E. A., General Electric Report, G. E. - TM 65-9-14 (1965).
9. Ledoux & Company, work carried out for General Electric, ANPD (1964).
10. Hibbits, J. O., and Schaefer E. A., General Electric Report, G. E. - TM 65-9-14 (1965).
11. Trumov, V. K., Kooba, L. M., Spitsyn, V. I., Doklady Akad. Nauk SSSR, No. 1, 114.
12. Juenke, E. F., and Bartram, S. F., Acta Crystallographica, 17(5)618 (1964).
13. Rothwell, E. J., Nucl. Mat. 6, 229 (1962).

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V. SPECTROGRAPHIC DETERMINATION OF TRACE IMPURITIES IN TUNGSTEN-URANIA-YTTRIA MIXTURES USING DIRECT-CURRENT ARC EXCITATION IN ARGON

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SUMMARY

An economical method employing argon chamber excitation has been developed and evaluated for the spectrographic determination of trace metallic impurities in a matrix of tungsten-urania-yttria. Of 15 selected impurities representing various excitation types, most are determinable at 2 ppm or less with a single procedure in which silver chloride carrier is added. Tantalum is very refractory in this matrix and is not excited even at the 1000 ppm level. A 22-foot Eagle spectrograph, with an inverse linear dispersion of 2.7\AA per millimeter in the first order, was applied to this study. Standard samples were synthesized from high purity constituents. The spectrographic procedure, which uses densitometric measurements and calibration curves, was developed for economic coverage of the selected elements and best precision of measurement.

INTRODUCTION

The fuel element development program at NASA Lewis Research Center continues to challenge the capabilities of analytical methods. The need exists for lower cost methods which require less sample and can cope with the complications of new and varying matrix mixtures.

The spectrographic techniques previously developed at the Oak Ridge Gaseous Diffusion Plant (ref. 1) provide coverage of 61 metallic elements. But this coverage requires 11 analytical procedures, and because chemical separations are necessary, sample size requirements total about 30 grams. These methods were developed for mixtures of tungsten and urania.

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The primary objective of the present study was to develop analytical procedures for purity control of fuel element materials which are more economical in terms of analytical effort and amount of sample required. The experimental approach was restricted to the use of emission spectra produced in a direct-current arc discharge in argon at reduced pressure and incorporated the metal cathode technique. This follows the general approach reported by Gordon of NASA (ref. 2). For the present evaluation, the matrix of interest was new - a mixture of tungsten, urania, and yttria powders. The elemental coverage was limited to 15 selected elements, representing a variety of excitation types. Because of the variety of excitation types, it is expected that many other metallic elements also will be determinable by the procedure developed. The development was carried out to establish optimum conditions for the direct detection of the specified trace elements at concentrations of 5 ppm or less, the establishment of optimum conditions for achieving the best precisions, and the quantitative calibrations based on synthetically prepared standards. The material of this paper is conveniently presented in five major sections, which describe the equipment, the preparation of standard samples, the spectrographic procedure, the important parameters of the procedure, and the results of the study.

This work was performed under NASA sponsorship (William A. Gordon, NASA Project Manager) at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

The authors wish to thank G. S. Petit and T. Kwasnoski of the ORGDP staff for the preparation of the high purity UO_2 and for the planning and guidance in the preparation of the standards. The authors are especially grateful to C. W. Weber for his administration of this project and his many helpful suggestions.

EQUIPMENT

A Spex Industry (Model 9700) controlled atmosphere chamber, shown in figure V-1, was used for this evaluation. The chamber, which consists of a Pyrex cylinder with stainless steel end plates, is gas-tight, permitting operation in special atmospheres either above or below atmospheric pressure. Both of the ground ends of the glass cylinder were polished to permit a vacuum seal against the Viton elastomer rings without grease. Silicone grease, previously applied, introduced a large and erratic blank, which prevented sensitive measurement of silicon. A quartz window, at the end of the side arm, transmits the ultraviolet radiation; and the side arm, which removes the window from the immediate vicinity of the arc, reduces deposits on the window. Up to 11 sample electrodes may be loaded at one time, each sample being moved to the arcing position by rotating an internal turntable from the outside with a gear-and-shaft seal arrangement.

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The counterelectrode is also adjusted from the outside with a screw-and-bellows seal. A shield, positioned horizontally over all electrodes except the one being arced, prevents cross contamination.

The vacuum system, shown schematically in figure V-2, consists of a mechanical pump connected to the chamber with 3/4-inch copper tubing. A 5/8-inch valve in the line controls the vacuum. The chamber pressure is measured with a 10-turn gage, 0 to 1000 millimeters of mercury, (catalog Number AI 101, Appleby and Ireland Limited, Basingstoke, Hampshire, England). For the micron pressure region, a thermocouple gage is used.

The samples are excited with a 0- to 60-ampere direct current power supply; an image of the arc, after masking out the glowing electrodes, is focused on the grating of the spectrograph. A two-step sector provides transmissions of 20 and 100 percent.

The spectrograph is a 22-foot Eagle instrument (ref. 3), using a concave grating ruled with 15 000 lines per inch over a $5\frac{1}{4}$ inch surface, and blazed for the first order ultraviolet region to provide an inverse linear dispersion of 2.7 Å per millimeter. Of course, any spectrograph with equivalent dispersion and resolution, and blazed for the region of interest, may be used.

The photographic plates are processed and read with standard commercial equipment.

PREPARATION OF STANDARD SAMPLES

The method for standard preparation is shown in figure V-3. Appropriate amounts of tungsten, UO_2 , and Y_2O_3 were weighed to provide a mixture containing 74.5 percent W, 23.3 percent UO_2 , and 2.2 percent Y_2O_3 (by weight). The materials were selected to give maximum purity at a reasonable cost. After blending and reducing in hydrogen at 900° C for 1 hour, spectrochemically pure oxides of the 15 selected elements were added and blended to provide a 1000 ppm master standard. Successive dilutions of the master standard with additional matrix provided the individual standards at the 1, 2, 5, 10, 20, and 50 ppm levels.

SPECTROGRAPHIC PROCEDURE

The spectrographic procedure starts with preparing the sample for arcing, and figure V-4 shows the controlled atmosphere chamber in the open, or loading, position. The empty electrodes are prearced in argon at 46 amperes for 40 seconds: the conditions being essentially the same as those used in arcing the sample. The carrier, consisting of 2 milligrams of AgCl , is weighed into the prearced electrode, and 250 milligrams of

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the sample is weighed on top of the AgCl. The sample is then tapped down in the electrode by tapping the bottom of the electrode against the table top.

The electrodes, which are of the cup pedestal type (Ultra Carbon type 7376 with center post removed), are positioned in the controlled atmosphere chamber by inserting the base part of each electrode into its supporting collet so that the top of the electrode base is flush with the collet. This positioning aligns the electrode with the optical system of the spectrograph and the electrode mask. The chamber then is closed and evacuated to an absolute pressure of 25 microns or less, flushed twice, and brought to 350 millimeters of mercury (absolute) with argon.

Each electrode is arced using a programed current of 3.5 amperes for 20 seconds and 11.5 amperes for 20 seconds, followed by 46 amperes for 40 seconds. In practice, the 46 ampere value is set with the current adjustment on the power supply; the 3.5 and 11.5 ampere currents are then obtained with the same current adjustment but with the "low" and "medium" range settings of the power selector switch.

The metal counterelectrode (private communication from W. A. Gordon of NASA Lewis Research Center), which is a tantalum ball at the end of a tantalum wire protruding from a graphite rod, is prepared in advance by inserting a length of 0.030-inch-diameter tantalum wire in the end of a drilled 1/8-inch graphite rod. The wire is cut about 0.4 inch from the end of the graphite rod, and the electrode is arced in argon at the current used for the analysis (46 amps) until the ball is formed.

The electrode is positioned for a 5-millimeter analytical gap. Since the electrode is hardly consumed in argon, it requires only minor adjustment during the arcings and is reused from sample to sample.

Spectrum analysis number 1 plates were used in this study and were processed and read using standard techniques. The measured optical densities of the spectral lines and of the background were converted to relative intensities, using emulsion calibration data and a calculating board (ref. 4). The average of the background intensities, measured on each side of the spectral lines, was subtracted from the measured line intensities, and the background-corrected line intensities or intensity ratios were plotted on log-log paper as a function of the element concentration in parts per million. The choice between using the elemental line alone or the ratio of the line to the silver internal standard line (2929 Å) was predetermined for each element, based on the precision evaluated at the 2 and 50 ppm levels. This will be further discussed later.

IMPORTANT PARAMETERS OF SPECTROCHEMICAL PROCEDURE

The development of the spectrochemical procedure for the W-UO₂-Y₂O₃ mixture had a two-fold objective: (1) to detect as many of the selected elements as possible at 5 ppm

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or less, and (2) to determine the elements with the best possible precision. In practice, the sensitivity and precision is limited by interfering excitation of the very complex spectrum of uranium in the matrix. The continuum-type background, which would probably be the factor limiting the sensitivity in the absence of uranium, was, comparatively speaking, not a problem. The continuum was not strong, and a correction was easily made. Of the other two matrix elements, tungsten did not excite, and the relatively simple spectrum of yttrium was seen but did not interfere with the elements sought.

To determine the optimum conditions for exciting the trace elements without excessive excitation of interfering uranium, a number of parameters were examined. The following 26 carrier combinations were examined:

Carriers with sample on top:

- 2 mg AgF
- 5mg LiF
- 5 mg Li_2CO_3
- 2 and 5 mg NaCl
- 2 and 5 mg Ga_2O_3
- 2 and 5 mg Ge metal
- 4 mg AgCl:LiF, 1:1
- 12 mg graphite:AgCl, 3:1
- 2, 5, 10, and 20 mg AgCl:AgF, 4:1

Carriers mixed with sample:

- 2, 5, 10 and 20 mg AgCl

Carrier on top of sample:

- 2 mg AgCl

The carrier is one of the more important parameters. Without a carrier, very poor sensitivity was observed. Of the 21 carriers evaluated with the carrier in the bottom of the electrode and the sample on top, 2 milligrams of AgCl was optimum, providing the best sensitivity without interfering uranium excitation. The 2, 5, 10, and 20 milligrams of AgCl mixed with the powdered sample and the 2 milligrams of AgCl placed on top of the sample showed no further improvement in the intensity of the trace elements relative to the uranium background.

The following important parameters were examined:

Carriers

Tapping and programed arc current

Depth of electrode cup

Arc current

Arc gap

Sample size

Entrance slit width and photographic plate

Exposure time (moving plate study)

Matrix effect

It was found that the position of the sample in the electrode relative to the arc affects the excitation of the trace elements and the excitation of the uranium in the matrix. To obtain the reproducible excitation of the impurity elements, without excitation of the uranium, it was necessary to position the sample in the bottom of the electrode and to maintain the sample in this position while arcing. The initial positioning was obtained by tapping the bottom of the electrode against the top of the table. Maintaining the sample at the bottom during arcing was achieved with a programed arc current of 3.5 A for 20 seconds, 11.5 A for 20 seconds, and 46 A for 40 seconds. Direct application of the high current caused the sample to be lifted from the bottom of the electrode, making analysis impossible because of heavy, and varying, interfering uranium excitation. The programed arc current, in which the sample is heated slowly, evidently provides controlled, rather than explosive, degassing of the sample.

Uranium background also was prevented with boiler caps. Since adequate control of the uranium background was achieved with the programed arc current, the boiler cap technique was not further pursued. Also, the depth of the electrode cavity is related to the positioning of the sample in the electrodes relative to the arc. This parameter was evaluated with cavity depths of 4, 5, and 6 millimeters; the 6 millimeters is the regular electrode depth. Increasing uranium background, obtained with decreasing depth, masked out any gain in sensitivity that may have resulted from bringing the sample charge closer to the arc. Since the uranium excitation is not excessive with the regular 6-millimeter electrode depth, greater depths were not examined. A few other electrode types also were examined with essentially the same results.

Tests with both higher and lower programed arc currents indicated significantly better precisions at higher currents. The arc current program of 3.5, 11.5, and 46 A for respective periods of 20, 20, and 40 seconds, as adapted for the procedure, indicated a standard deviation of ± 14 percent, compared with ± 24 percent for a lower current program consisting of 3 A for 20 seconds, 9 A for 20 seconds, and 35 A for 80 seconds.

(These preliminary precisions are the average values for all elements at the 10 ppm level, expressed for single determinations.)

Arc gaps of 5 and 12 millimeters were examined and compared. The 12-millimeter gap was examined in three 4-millimeter increments (equivalent to the solid angle subtended by the optical system of the spectrograph), using separate arcings for each increment. For the 5-millimeter gap, the bottom 4 millimeters were measured. The top and middle increments of the 12-millimeter gap showed relatively little sensitivity; however, the bottom 4 millimeters, nearest the sample electrode, provided higher sensitivities but poorer precisions (by a factor of about $1\frac{1}{2}$) than the bottom 4 millimeters of the 5-millimeter gap. In addition to the poorer precision, the larger gap had a tendency to arc the shield inside the chamber, making analysis unreliable. Because of this tendency and the poorer precision of the larger gap, the 5-millimeter gap was selected for the procedure.

The 250-milligram sample size with 2-milligram AgCl carrier, selected for the procedure, is probably nearly optimum in terms of sensitivity, interference from uranium excitation, and economy of sample. A larger sample would probably be equivalent to reducing the electrode depth by bringing the sample closer to the arc. Several 100-milligram samples with the regular 2-milligram AgCl carrier and one 100-milligram sample with a 20-milligram AgCl carrier resulted in poorer sensitivity with 2-milligram AgCl and excessive uranium interference with 20-milligram AgCl.

A 36-micron entrance slit with SA1 photographic plates was used, the combination of which provides background-limiting measurements. Using the SA1 photographic plates, tests with a 25-micron slit indicated intensity-limiting measurements, while a 50-micron slit resulted in excessive background.

To determine the optimum exposure time for best sensitivity and precision, moving plate studies with 20-second rack down intervals were made for the 5, 10, 20, and 50 ppm levels; the 50 ppm results are shown in figure V-5. The data were collected using programed 35-A arc current excitation. Each horizontal line through a 20-second interval indicates a measurable spectral line intensity for that 20-second rack down exposure. The approximate time of the peak intensity and of half the peak intensity are indicated by a circle and triangle, respectively.

The results indicate that most of the elements are completely excited during the first 20 seconds at 35 A, and that a total exposure period of 120 seconds includes complete excitation periods for all of the elements except copper, for which a large percentage of the excitation is included. The sustained silicon intensity is from contamination by silicone grease in the chamber. This has since been eliminated. Visual examination of the moving plates indicated that essentially all the continuum background was excited during the first 20-second interval at 35 A, coinciding with the peak excitation of the impurity elements. Photographic recording from the beginning of the low amperage

excitation should permit measurement of highly volatile metals in the W- UO_2 - Y_2O_3 matrix, without significant background limitation. Silver, the carrier element, appears adequate, since it volatilizes at a good rate throughout the exposure.

Since most of the impurity excitation occurred during the first 20 seconds at 35 A, it was concluded that changing the high current excitation from 80 seconds at 35 A to 40 seconds at 46 A, to provide better precision, would present no sacrifice in excitation of the impurities. This was borne out by obtaining no loss in sensitivity.

Figure V-6 shows similar results for the 5 ppm level. The results at the 10 and 20 ppm levels were essentially the same.

Optimizing the procedure according to the findings of these tests, all 15 elements except zirconium and tantalum were seen in standards containing 5 ppm or less. Zirconium was seen in the 10 ppm standard, while tantalum could not be seen even at 1000 ppm. The effect of the matrix components on the determination of these elements was evaluated by preparing 1000 ppm tantalum standards in UO_2 , in tungsten, and in a UO_2 -W mixture. Similar zirconium standards were prepared at the 5 ppm level. Both elements were readily excited with 2 milligrams of AgCl carrier in W, but not in either the UO_2 or the UO_2 -W mixture, indicating that the UO_2 was suppressing both elements. It may be necessary, therefore, to develop a separate procedure for determining tantalum and similarly refractory elements in matrices containing UO_2 .

RESULTS

The limits of detection are shown in table V-I. The first column lists the 15 selected elements, and the second column, the wavelengths of the spectral lines used. Of the six standards examined (1, 2, 5, 10, 20, and 50 ppm), column 3 shows the lowest standard in which the spectral line of the element was seen. For those elements showing a significant spectral line intensity in the blank, estimates of the concentration were made by applying Harvey's "Addition Method of Analysis" (ref. 5) and are listed in table V-I as the lowest standards seen. These are indicated by an asterisk.

The last column of the table shows the estimated limits of detection, based on a line-to-background ratio of 0.3. These limits of detection were estimated by expressing 0.3 of the background intensity in ppm, using extrapolated portions of the calibration curves. (For each calculation, the average of six measurements of the background, three on each side of the respective spectral line, was used.)

The precision, shown in table V-II on an absolute and on a relative basis, was evaluated at the 2 and 50 ppm levels. The precision for each element is the standard deviation for a single-electrode determination, based on 10 repeat determinations of the 2 ppm standard and 11 determinations of the 50 ppm standard.

[REDACTED]

The precision was evaluated for the relative intensity of the impurity spectral line and for the intensity ratio of the impurity line to the 2929 Å silver line. In the latter case, the added AgCl serves both as carrier and internal standard. Better precision was obtained using the intensity ratio for all elements examined except magnesium, silicon, and vanadium. For those three elements, the precisions and calibrations were obtained using relative intensities.

The average precisions of ± 37 and ± 18 percent for the 2 and 50 ppm levels, respectively, were determined by averaging the relative precisions of all elements examined.

Calibration curves (working curves) for the individual elements were prepared. Figure V-7 shows a working curve for chromium in which the intensity ratio of the 2843 Å chromium line to the 2929 Å silver line is plotted against ppm chromium. The 1/2 ppm chromium in the matrix is included in the calibration by equivalent increases in the nominal concentration of the standards. The 1 ppm standard is plotted as $1\frac{1}{2}$, the 2 as $2\frac{1}{2}$, etc.

Each point, except those for 2 and 50 ppm, represents the average of three determinations. The 2 and 50 ppm points, indicated by double circles, are the average of 10 and 11 determinations, respectively. The best straight line was drawn through the points, with added weight given the 2 and 50 ppm points. Similar calibration curves also were prepared for iron, gadolinium, and zirconium, appropriate blank corrections being included where applicable.

For those elements having intensity ranges greater than the usable range of the photographic emulsion, double calibration curves were used. The higher concentrations were calibrated using either a sector with a 20 percent transmission or a weaker spectral line. Figure V-8, which shows a calibration for calcium, shows the application of the 20-percent sector for the higher concentration. The $1\frac{1}{2}$ ppm matrix blank is included in the calibration. Similar calibration curves were prepared for aluminum, dysprosium, europium, and titanium.

The use of a weaker line for the higher concentrations is shown in figure V-9, which is a calibration for copper. A weaker line for the higher concentration also was used for manganese.

Figure V-10 shows the calibration for vanadium, in which relative intensity is used instead of intensity ratio. As discussed earlier, relative intensity measurements provided better precision for vanadium, and for magnesium and silicon. Relative intensity plots were used for these three elements.

CONCLUSION

A complete presentation of the work conducted in this program is being prepared as a formal project report by the Oak Ridge Gaseous Diffusion Plant. In concluding this

brief discussion, I would like to say that the objectives of this development program were met in achieving an economical procedure for determining trace impurities in a defined matrix of tungsten-urania-yttria.

The matrix has a pronounced effect on the excitation of some impurities. Of the 15 elements studied, only tantalum was severely limited in sensitivity. A separate procedure may be required for measurement of such refractories. With the further exception of zirconium, which has a limit of detection of 10 ppm, all the other elements studied can be measured at 5 ppm or less. Since the matrix was limited to a fixed ratio of constituents, the reliability of calibration data would need to be confirmed for application to other mixtures.

Appropriate techniques should be established to permit the handling of mixtures of various physical states. Tungsten-coated and compacted materials, as well as powder blends, might be universally accepted as samples after a proper oxidation-reduction treatment. Developing adequate sample preparation methods is needed for reliable measurement of these selected elements and, eventually, a much broader scope of impurities.

REFERENCES

1. Weber, C. W., and Kwasnoski, T., Editors, Determination of Impurities in Tungsten-Uranium Dioxide Mixtures, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, Feb. 19, 1965 (K-1621, Revised) (NASA CR-54275).
2. Gordon, W. A., Use of Temperature Buffered Argon Arc in Spectrographic Trace Analysis, N.A.S.A., Lewis Research Center, Cleveland, Ohio, January, 1965, (NASA TN D-2598).
3. Lee, T., "The Design and Construction of a 22-Foot Direct-Reading Optical Spectrometer," Applied Spectroscopy, 8, 174-207 (1954).
4. Hallowell, A. L., Operation of Spectrographic Calculator, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, April 30, 1954.
5. Harvey, Charles E., Spectrochemical Procedures, Applied Research Laboratories, Glendale, California, 1950, pp. 218-226.

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TABLE V-I. - LIMITS OF DETECTION

| Element | Wavelength, Å | Lowest standard seen, ppm | Limit of detection, ^a ppm |
|---------|------------------|------------------------------|---|
| Al | 3082 | 1 | 0.05 |
| Ca | 3179 | ^b 1.5 | 1 |
| Cr | 2843 | ^b .5 | .1 |
| Cu | 3273 | ^b .5 | .08 |
| Dy | 3531 | 2 | .4 |
| Eu | 3688 | 1 | .1 |
| Fe | 2994 | ^b 5 | 1.2 |
| Gd | 3350 | 1 | .7 |
| Mg | 3838 | 1 | .3 |
| Mn | 2949 | 1 | .4 |
| Si | 2881 | ^b 4 | .3 |
| Ta | (c) | (c) | (c) |
| Ti | 3349 | ^b .5 | .4 |
| V | 2924 | ^b 1 | 1 |
| Zr | 3391 | 10 | 10 |

^aCalculated equivalent to line intensity of 30 percent above background.

^bBlank in matrix.

^cNot seen in presence of UO₂.

TABLE V-II. - PRECISION

| Element | 2 ppm standard | | 50 ppm standard | |
|---------|----------------|----------------------|-----------------|----------------------|
| | Absolute | Relative, percent | Absolute | Relative, percent |
| Al | 2±0.7 | ±35 | 50±5.5 | ±11 |
| Ca | 3.5±0.5 | ±14 | 51.5±8 | ±16 |
| Cr | 2.5±0.5 | ±20 | 50.5±14.5 | ±29 |
| Cu | 2.5±0.6 | ±24 | 50.5±11 | ±22 |
| Dy | 2±0.6 | ±30 | 50±8 | ±16 |
| Eu | 2±0.4 | ±20 | 50±15 | ±30 |
| Fe | 7±2.8 | ±40 | 55±10 | ±18 |
| Gd | 2±1.5 | ±75 | 50±4 | ±8 |
| Mg | 2±1.3 | ±65 | 50±5 | ±10 |
| Mn | 2±1.3 | ±65 | 50±10 | ±20 |
| Si | 6±2 | ±33 | 54±3 | ±6 |
| Ti | 2.5±0.8 | ±32 | 50.5±17.5 | ±35 |
| V | 3±1 | ±33 | 51±6 | ±12 |
| Zr | ----- | --- | 50±10.5 | ±21 |
| | | Av, ±37 | | Av, ±18 |

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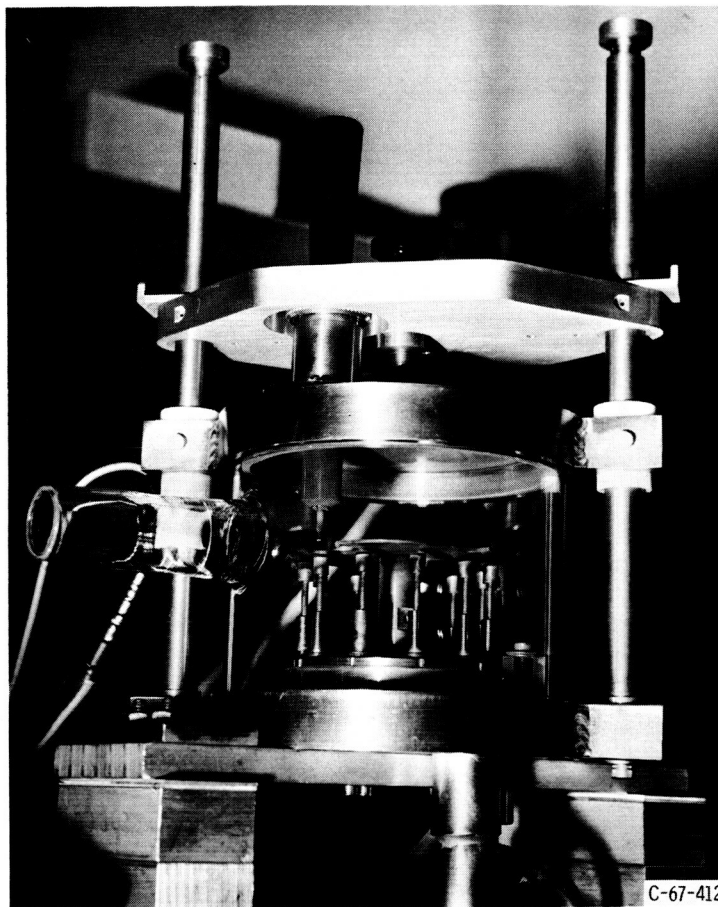


Figure V-1. - Controlled atmosphere arc chamber.

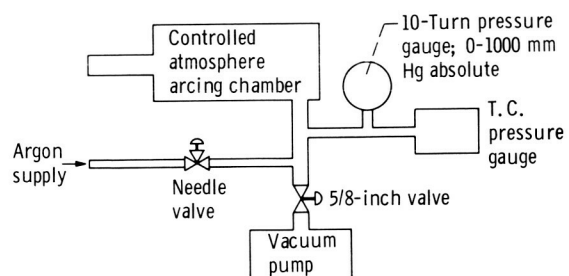


Figure V-2. - Vacuum system.

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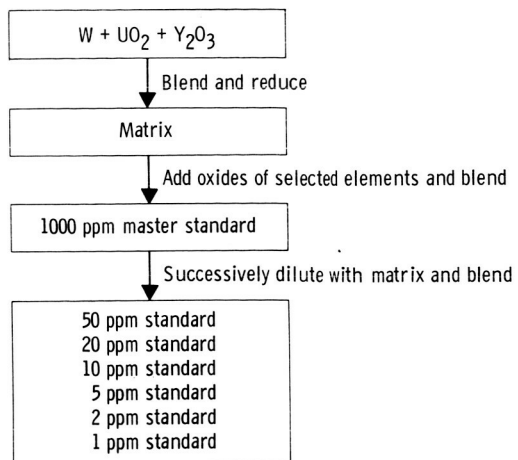


Figure V-3. - Flow chart for standards.

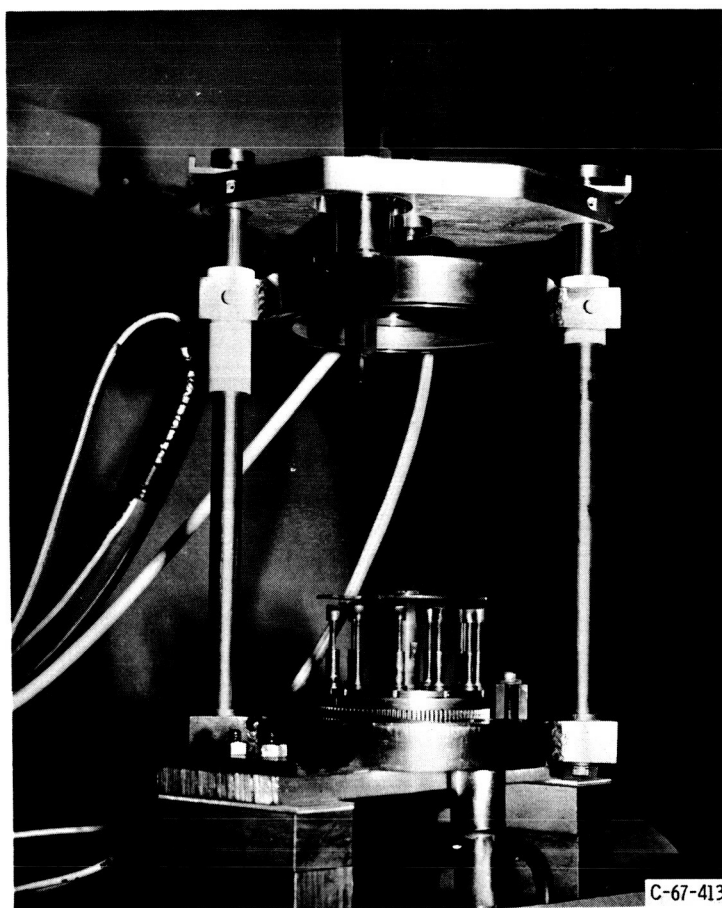


Figure V-4. - Controlled atmosphere arc chamber; open for loading.

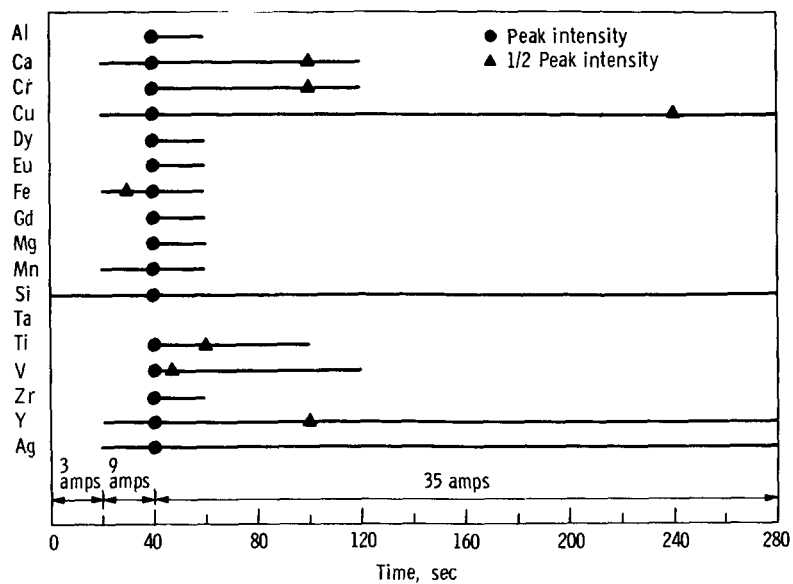


Figure V-5. - Moving plate data - 50 ppm level.

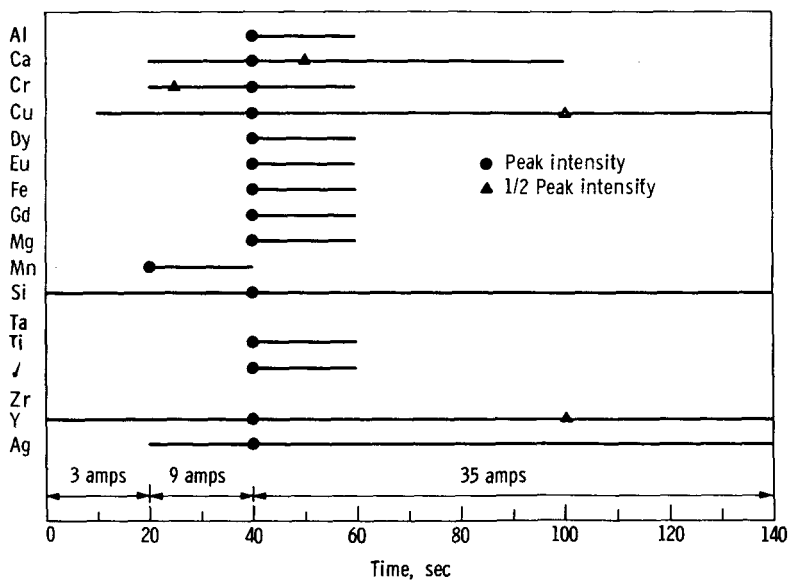


Figure V-6. - Moving plate data - 5 ppm level.

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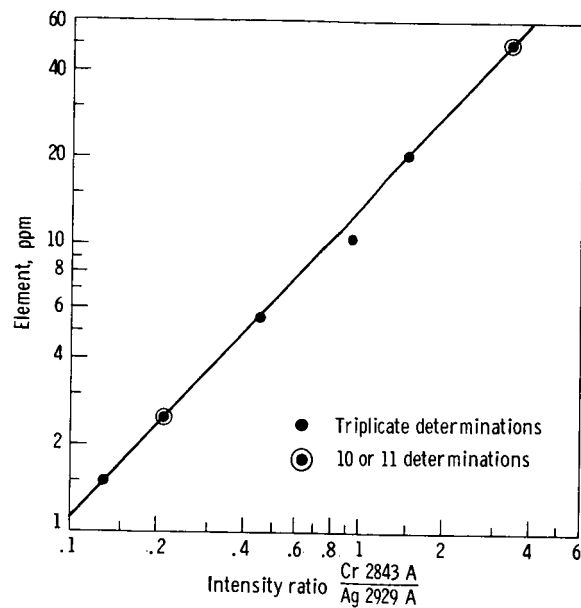


Figure V-7. - Calibration for chromium.

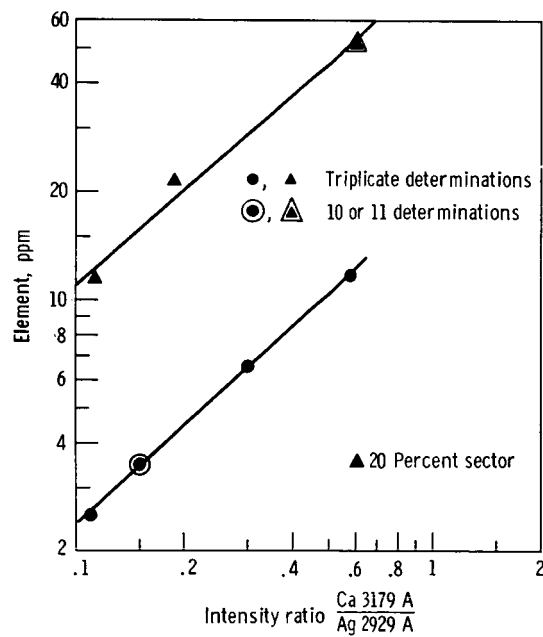


Figure V-8. - Calibration for calcium.

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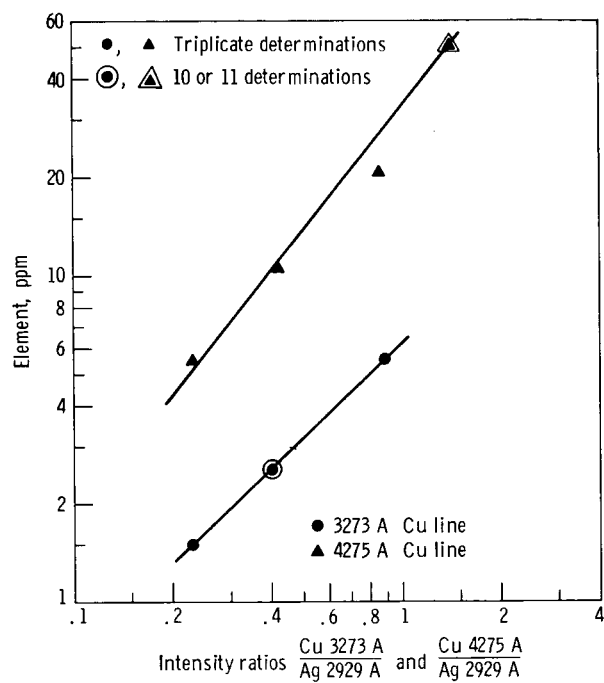


Figure V-9. - Calibration for copper.

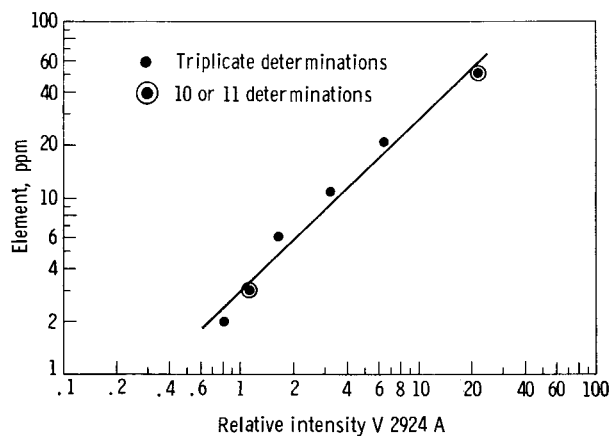


Figure V-10. - Calibration for vanadium.

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VI. DIRECT DETERMINATION OF OXYGEN IN URANIUM DIOXIDE

MATERIALS BY INERT GAS FUSION

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SUMMARY

A carbon-reduction method that has been shown to be applicable to the direct, macro-determination of oxygen in oxides such as Fe_2O_3 , SiO_2 , Al_2O_3 , Cr_2O_3 , UO_2 , Ta_2O_5 , and TiO_2 with an average error in precision of <1 percent has been applied to the analysis of UO_2 composite materials. Sample sizes ranged around 300 milligrams. About 100 milligrams of CO_2 produced by the procedure were measured gravimetrically.

Techniques necessary to prevent sample loss by entrainment or by metal-bath spatter, during carbon reduction of the sample, involved keeping the graphite crucible covered and maintaining its temperature within predetermined limits.

INTRODUCTION

As experimental work expands in scientific fields involving refractory nuclear fuels, ceramics, meteorites, rocks, and other solid substances containing mixtures of metal oxides, the need increases for a precise method by which the oxygen content may be measured directly rather than by difference. Preferably the method should be applicable in a macrorange so that the sample size might be large enough to favor homogeneous sampling of heterogeneous materials and so that the measurement data might contain enough significant figures to afford good precision in the calculated results.

This paper describes the extension of the inert gas fusion method toward the macro-range. Sample sizes ranged from 100 to 400 milligrams. The quantity of CO_2 produced by the procedure was about 100 milligrams. It was collected in weighing tubes and measured on a standard analytical balance.

The chief modifications made to the inert gas fusion procedure, as it is usually applied to microquantities of oxygen in metals, were control of the rate of formation of CO

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in the graphite crucible, oxidation of CO to CO₂ by hot copper oxide rather than by rapidly depleted iodine-pentoxide oxidizers, and gravimetric (rather than manometric or conductometric) measurements of the CO₂.

The paper is based on work performed under the auspices of the U. S. Atomic Energy Commission.

The authors are grateful to Adolph Venters, John Marsh, and John Stoessel for microanalyses of UO₂ samples.

EXPERIMENTAL

Apparatus

As illustrated in figure VI-1, the analytical train consisted of a source of pure inert gas (helium or argon), a water-cooled fused-silica furnace tube containing a covered graphite crucible inductively heated by a 10-kilowatt generator, a copper oxide furnace, a desiccating tube, a weighing tube, and an exhaust bubbler. As a convenient accessory, a manometric train (also shown in fig. VI-1) was attached to be operated either in series with or in place of the gravimetric train. It consisted of a Schutze reagent tube (ref. 1), a capillary trap manometer, and a vacuum line.

Figure VI-2 illustrates the crucible and lid. Sixteen holes, 1/16 inch in diameter and equally spaced, were drilled radially into the side of the lid as shown. To facilitate easy assembly and disassembly, the lid was made to fit loosely in the crucible, and its lower edges were slightly rounded. The crucible and lid were fabricated from a 3/4-inch-diameter extruded graphite rod, grade AUC, supplied by the National Carbon Co., N. Y. Suitable tongs were fabricated for reaching in from the top of the furnace tube to remove the crucible and lid.

The silica tube (3-cm o.d. by 25-cm long) containing CuO in wire form was maintained at 450° C. Oxygen was introduced by the three-way stopcock at the entrance of the tube for reoxidation of reduced copper.

The CO₂ weighing tube (Schwartz absorption type with ball-and-socket side tubes), manufactured by Corning Glass Works Number 98250, was filled to three-fourths of its volume with Ascarite, followed by one-fourth volume of Anhydrone. Glass wool plugs were inserted at each end, and glass wool or exploded mica was interspersed with the Ascarite to minimize clogging of gas flow after several hundred milligrams of CO₂ had been absorbed. The weighing tube was attached to a bypassing four-way stopcock by ball-joint linkages for convenient installation and support. The ball joints touching the weighing tube contained no grease. The tube was preceded by an identical one filled with Drierite and Anhydrone and was followed by an exhaust bubbler by which the rate of gas flow was monitored.

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The components of the manometric train shown in the diagram are modified units of equipment described earlier by Smiley (ref. 2).

Platinum capsules, into which oxide samples were weighed before dropping into the crucible, were 0.344 inch in length and were made from 0.180-inch-outside-diameter tubing, 0.005 inch in wall thickness. One end of each capsule was closed by a metal-spinning process. After weighing in the sample, the other end was closed by crimping with pliers.

The output power of a 10-kilowatt induction heating generator, manufactured by Induction Heating Corp., N. Y., was controlled by a Variac transformer on the 220-volt, single-phase circuit, feeding the primary coils of the input transformer. The power was continuously variable in a range sufficient to produce crucible temperatures of 600° to 2100° C.

Procedure

Place a crucible and lid, which have been previously baked out for 5 minutes at 2000° C in an inert atmosphere, on a tungsten wire support in the furnace tube and add 7 grams of platinum. Heat for 10 minutes at about 2000° C with inert gas flowing through the train and out the bubbler but bypassing the weighing tube. Heat an additional 10 minutes with the gas stream flowing through the weighing tube. Allow the line to flush 5 minutes before removal of the weighing tube. Close inlet stopcock of weighing tube. Remove the weighing tube from the train allowing it to come to atmospheric pressure before closing the outlet stopcock. Wipe the weighing tube, first with a damp cloth and then with chamois leather. Remove static charge on the tube by exposing it to a Tesla spark coil. Repeat 10-minute heat cycle until the weighing tube reaches a constant weight.

When the weighing tube has been brought to constant weight, the cooling water in the silica furnace tube is shut off and heated by turning on the 10-kilowatt generator and inductively heating the crucible until water in the cooling jacket becomes warm to the touch.

Remove the optical-window cap on the furnace tube and, with inert gas flowing out, reach in with appropriate tongs and remove the crucible. Replace the cap on the furnace tube, and set the crucible in an appropriately designed glass holder, placed on a clean sheet of aluminum foil on the laboratory bench. Lift the crucible lid, introduce a weighed sample contained in a platinum capsule, and then return the closed crucible to the tungsten support in the furnace tube. Locate the supporting member of a viewing mirror (for optical pyrometer readings) over the furnace tube cap in such a way as to hold it down securely during the subsequent procedure. Evacuate silica furnace tube to a pressure reading on a manometer of 2 to 5 millimeters.

Manipulate the stopcocks to direct a stream of about 150 cubic centimeters per minute through the reaction tube, CuO furnace, desiccating tube, weighing tube, and bubbler. Or, instead of using the bubbler, the manometric train may be operated in series with the gravimetric train, as a precaution against incomplete removal of CO₂ in the weighing tube. In this case, the gas flow should be throttled at the inlet stopcock of the capillary manometer.

Set the power to the induction heating coil such that the temperature of the crucible lid is raised to a point which by previous calibration corresponds to a temperature inside the crucible of about 1550° C. (The calibration is conveniently made by temporarily using a lid with a vertical, 52-mil peep hole drilled in it. Simultaneous readings can be made of the inside temperature and of the lid temperature for various settings of the Variac that controls the input voltage to the induction heater.) If, before such a temperature is reached, smoke is seen to be evolved from the crucible, immediately decrease the input power until the smoking is diminished almost to extinction. Hold at this setting for 15 minutes. Raise the temperature of the lid about 150° C, and hold for 10 minutes. Finally boost the power to produce a temperature of about 2000° C inside the crucible, and hold for 5 minutes. Shut off the power to the work coil, and turn off the cooling water to the furnace tube to ensure that the inside walls will be warm when the furnace tube is subsequently opened for the addition of the next sample. Allow the line to flush 5 minutes before removal of the weighing tube.

Disconnect and weigh the weighing tube, using the technique just described. From the total amount of CO₂ that is measured, deduct the prevailing blank (usually about 0.3 mg) that is obtained by proceeding through all the steps of the analysis, using an empty platinum capsule for the sample.

RESULTS

It was necessary to adjust and control the crucible temperature more precisely in the determination of milligram amounts of oxygen than is normally required for microgram quantities by the inert gas fusion method. The need for the control of the rate at which CO is produced inside the crucible may be illustrated as follows. An oxide sample of sufficient size to produce the conveniently weighable quantity of 100 milligrams of CO₂ is converted to about 350 cubic centimeters of CO, not including the volume of gaseous metal vapor, which must escape from the interior of the crucible (at 1600° C) through the holes in the lid. Certainly, if the temperature is raised too high or too rapidly, the gas pressure inside the crucible can increase sufficiently to dislocate the lid and to blow unreacted sample particles out of the crucible.

During the course of the investigation, more and more effort was devoted toward

[REDACTED]

operation at the minimum temperature effective in the reduction of a given oxide within a 20-minute period. As might be expected, this minimum varied from one oxide to another, being slightly lower for W-UO₂ than for U₃O₈. Also, it was noted that the visual detection of smoke during the reduction of the oxides was usually accompanied by low results. When smoke appears during the reduction reaction, it may be assumed that CO is being released too rapidly and that some of the oxide dust particles are being carried away by entrainment (ref. 3). With these precautions in mind, some UO₂ composites were analyzed. The following tables (tables VI-1 to 7) illustrate the precision obtained for oxygen analysis by adhering to this procedure.

REFERENCES

1. Smiley, W. G., Nucl. Sci. Abstr. 3, 391 (1949).
2. Smiley, W. G., Anal. Chem. 27, 1098 (1955).
3. Holt, B. D. and Stoessel, J. E., Anal. Chem. 36, 1320 (1964).

TABLE VI-I. - RECOVERY DATA

ON U_3O_8 (NBS SAMPLE 950a)

| Oxygen content, percent | Recovery, percent |
|---|----------------------|
| 15.20 | 100.0 |
| 15.21 | 100.1 |
| 15.28 | 100.5 |
| 15.16 | 99.7 |
| 15.23 | 100.2 |
| 15.18 | 99.9 |
| 15.19 | 99.9 |
| 15.25 | 100.3 |
| 15.18 | 99.9 |
| Average | 100.1 |
| Relative standard deviation ^a | ±0.3 |

^aRelative standard deviation =

$$\frac{\sqrt{\frac{\sum d^2}{n-1}}}{\text{Average value}} \times 100.$$

TABLE VI-II. - PERCENT OF OXYGEN

IN UO_2 (METHOD OF ANALYSIS)

| Oxide sample | Oxidation to U_3O_8 | Macro-inert-gas fusion |
|-----------------------------|-----------------------|------------------------|
| 1 | ^a 12.37 | 12.38 |
| | ^a 12.32 | 12.32 |
| | | 12.39 |
| | | 12.33 |
| | | 12.34 |
| | | 12.37 |
| | | 12.36 |
| Average | | 12.36 |
| Relative standard deviation | | ±0.2 percent |
| 2 | ^b 11.85 | 11.85 |
| | | 11.84 |
| | | 11.82 |
| Average | | 11.84 |
| Relative standard deviation | | ±0.2 percent |

^aBy ANL Chemical Engineering Division.

^bBy ANL Chemistry Division.

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TABLE VI-III. - RECOVERY DATA OBTAINED

ON W- UO_2 COMPOSITES

| Sample (^a W + ^b UO ₂) | Oxygen content, percent | | Recovery, percent |
|---|-------------------------|------------------------|----------------------|
| | Calculated | Macro-inert-gas fusion | |
| 1 | 8.70 | 8.67 | 99.7 |
| 2 | 10.21 | 10.22 | 100.1 |
| 3 | 9.39 | 9.38 | 99.9 |
| 4 | 9.10 | 9.11 | 100.1 |
| 5 | 10.89 | 10.88 | 99.9 |
| 6 | 9.62 | 9.60 | 99.8 |
| Average | | | 99.9 |
| Relative standard deviation | | | ±0.2 |

^a0.28 Percent oxygen (inert-gas-fusion method).

^b11.85 Percent oxygen (oxidation to U_3O_8 and inert gas fusion methods).

TABLE VI-IV. - THORIUM OXIDE - URANIUM

OXIDE COMPOSITES

| Sample | Oxygen, percent | Difference between duplicates, percent |
|---|--------------------|---|
| 1 | 11.81 11.80 | 0.01 |
| 2 | 11.91 11.80 | .11 |
| 3 | 11.91 11.88 | .03 |
| 4 | 11.69 11.70 | .01 |
| 5 | 11.83 11.78 | .05 |
| Average difference | | 0.04 |
| Relative standard deviation of difference | | 0.5 percent |

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TABLE VI-V. - ZrO_2 - UO_2 COMPOSITES

| Sample, mole percent | Oxygen, percent | Difference between duplicates, percent |
|---|--------------------|---|
| 5 ZrO_2 -95 UO_2 | 12. 15 | 0. 04 |
| | 12. 19 | |
| 10 ZrO_2 -90 UO_2 | 12. 55 | . 03 |
| | 12. 52 | |
| 5 ZrO_2 -95 UO_2 | 12. 09 | . 03 |
| | 12. 12 | |
| 10 ZrO_2 -90 UO_2 | 12. 30 | . 05 |
| | 12. 25 | |
| Average difference | | 0. 04 |
| Relative standard deviation difference 0. 3 percent | | |

TABLE VI-VI. - RARE EARTH OXIDES- UO_2 COMPOSITES

| Sample | Oxygen, percent | Difference between duplicates, percent |
|---|--------------------|---|
| SmO_2 - UO_2 | 12. 30 | 0. 06 |
| | 12. 24 | |
| | 12. 09 | . 07 |
| | 12. 16 | |
| Eu_2O_3 - UO_2 | 12. 01 | . 00 |
| | 12. 01 | |
| | 12. 05 | . 00 |
| | 12. 05 | |
| Gd_2O_3 - UO_2 | 12. 09 | . 03 |
| | 12. 06 | |
| | 12. 21 | . 06 |
| | 12. 27 | |
| | 11. 90 | . 13 |
| | 11. 77 | |
| | 12. 08 | . 02 |
| | 12. 06 | |
| | 11. 86 | . 02 |
| | 11. 84 | |
| | 12. 29 | . 01 |
| | 12. 30 | |
| Average difference | | 0. 04 |
| Relative standard deviation of difference | | 0. 5 percent |

TABLE VI-VII. - Al_2O_3 - UO_2 COMPOSITES

| Sample | Oxygen, percent | Difference between duplicates, percent |
|---|--------------------|---|
| 1 | 12.23 12.28 | 0.05 |
| 2 | 12.34 12.14 | .20 |
| 3 | 12.61 12.43 | .18 |
| 4 | 11.93 11.86 | .07 |
| 5 | 11.85 11.83 | .02 |
| 6 | 12.55 12.74 | .19 |
| 7 | 12.00 12.05 | .05 |
| 8 | 12.44 12.54 | .10 |
| Average difference | | 0.11 |
| Relative standard deviation of difference | | 1.1 percent |

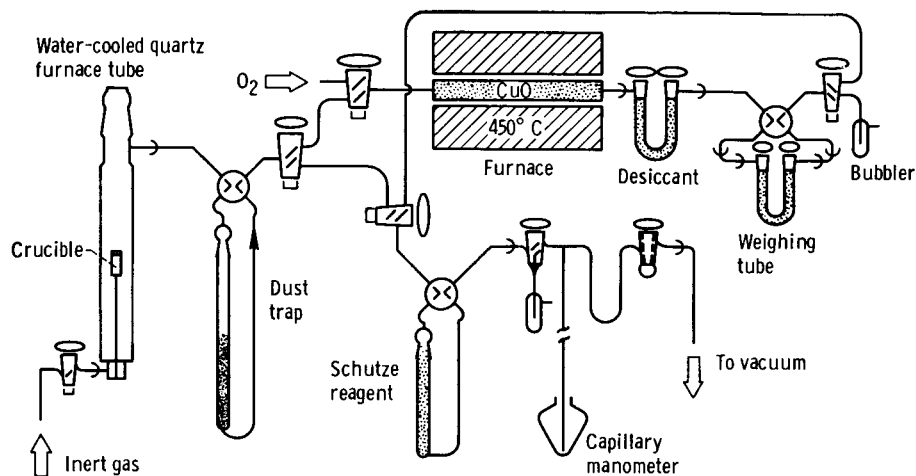


Figure VI-1. - Analytical train.

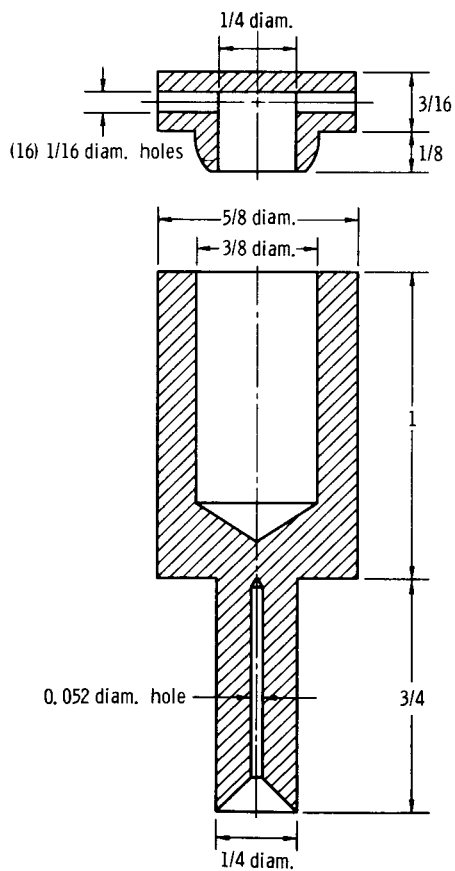


Figure VI-2. - Crucible and lid. (All dimensions in inches.)

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VII. ANALYTICAL METHODS FOR TUNGSTEN - URANIUM DIOXIDE MATERIALS

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SUMMARY

Methods were developed, or existing methods were modified, for the determination of chloride, fluoride, nitrogen, uranium, tungsten, cerium, yttrium, and rare earth oxides in tungsten - uranium dioxide materials. Pyrohydrolytic, ion-exchange, volumetric, and photometric techniques applicable to the tungsten-urania system are described.

INTRODUCTION

The following analytical techniques for tungsten, urania, and/or tungsten-urania systems are based on extensive experience in the field of uranium analysis and related fuel materials. The analytical procedures have been developed and validated to provide adequate analytical control of fuel product materials.

I - DETERMINATION OF CHLORIDE IN TUNGSTEN AND MOLYBDENUM (Procedure AC-C1-1B)

A. METHOD

1. Scope

This method is recommended for the determination of chloride in tungsten and molybdenum. It is applicable to such metals as niobium and vanadium and to UO_2 and W- UO_2 composites.

2. Summary of Method

The sample is fused with a flux and the chloride hydrolyzed at 850° C in a stream of moist oxygen. The volatilized HCl is absorbed in 30 ml of water, cooled, and treated with an excess of methyl alcohol and mercuric thiocyanate. Ferric ammonium sulfate is added, and the intensity of the resulting ferric thiocyanate, as determined by the amount of chloride present, is measured photometrically at 470 mμ.

B. APPARATUS

1. Burrell Electric Furnace, model H-2-9
2. Beckman model B Spectrophotometer with matched 5 cm cells
3. Quartz reaction tube
4. Quartz boats (3 by 5/8 by 3/8 in.)
5. Steam generator with immersion heater (Aminco Co.) number 1880
6. Beakers, 150 ml polypropylene

C. REAGENTS

Unless otherwise noted, all chemicals are reagent grade. Water is deionized, Grade A.

1. Ferric ammonium sulfate (6 percent)

Dissolve 60.0 grams $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2 \cdot 24\text{H}_2\text{O}$ and dilute to the mark in a 1-liter flask with 6N nitric acid. Allow to stand at least 24 hours. This solution is stable for several months if stored in a brown bottle.

2. Mercuric thiocyanate (1.5 percent)

Dissolve 7.5 grams Hg (SCN) in 500-ml methyl alcohol. Mix the reagent using a magnetic stirrer for at least 1 hour and filter through Whatman number 41 paper.

3. Nitric acid (6N)

4. Sodium chloride (20 μg Cl/ml)

Dry a 1-gram sample of reagent grade sodium chloride at 110° C for several hours and store in a desiccator. Transfer 0.0330 gram of the dry NaCl to a 1-liter flask and dilute to the mark with chloride-free water.

Zinc chloride may also be used as a standard. (0.1922 g $\text{ZnCl}_2/1$
= 100 μg Cl/ml)

5. Sodium molybdate-molybdenum trioxide flux

(a) Wash thoroughly all the apparatus required with deionized water and dry it quickly under an infrared lamp.

) [REDACTED]

(b) Transfer 113 grams of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ to a 500-ml platinum dish and gently heat with a Meker burner to dehydrate most of the $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$.

(c) Transfer the Na_2MoO_4 to a mortar and add 135 grams of MoO_3 , mix with a spatula, and then grind with a pestle.

(d) Transfer the mixture to a 500-ml platinum dish. Heat the dish gently in a hood for about 10 minutes with the low flame of a Meker burner; then increase the temperature until the bottom of the dish is at a dull red heat. Maintain this temperature for about 2 hours.

(e) Let the melt cool until the top has solidified. Then place the dish on one of two clean dry porcelain trays, and carefully spray a small stream of water on the outside of the dish until the melt has solidified completely.

(f) Invert the dish on the other tray, and tap to dislodge the cake.

(g) Break the cake into small pieces. Then transfer a few portions of the cake at a time to a clean dry mortar, and grind them to a coarse powder.

(h) Transfer the powder to a clean, dry, and air-tight storage bottle.

6. U_3O_8 (NBS950)

D. CALIBRATION

1. Take separate aliquots of standard NaCl solution containing 20, 40, 60, 80, and 100 μg of Cl_2 . Add the solution to 1.0 gram of U_3O_8 (NBS950) or scrap which has been cleaned by pyrohydrolysis in a quartz boat. Evaporate to dryness under a heat lamp.

2. Start the flow of oxygen saturated with water vapor and regulate the flow at 1 to 1.5 liters per minute (60 to 90 liters/hr).

3. Place the quartz boat into the quartz pyrohydrolysis tube which is maintained at 850°C .

4. Pass oxygen over the sample for 7.5 minutes and into 30 ml of H_2O in a 150 ml polypropylene beaker. The tip of the delivery tube should be below the surface of water.

5. Transfer the solution to a 50 ml volumetric flask and cool.

6. Add 5 ml methyl alcohol. Swirl to mix.

7. Add 2 ml each of ferric ammonium sulfate and mercuric thiocyanate. (After each addition, rinse the walls of the flask with water to insure thorough mixing.) Dilute to volume and mix.

8. Allow the solutions to stand for 15 minutes. Read the optical density against a 5-centimeter reference cell containing water.

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9. Construct a calibration curve plotting micrograms of chloride added versus the net optical density (corrected for reagent blank). Recheck this curve daily at three points.

E. PROCEDURE

1. Before conducting any analyses, the following daily precautions should be taken:

(a) A reference blank should be carried out to determine whether any reagent contamination has occurred. This optical density should correspond to the reagent blank. This will also serve to determine if the water has been contaminated.

(b) A complete "system blank" (without a sample) should be conducted. This is continued until the optical density corresponds to within 0.005 to 0.01 of the reagent blank.

(c) A flux blank should be determined by placing 2 grams of the $\text{Na}_2\text{MoO}_4\text{-MoO}_3$ flux in a quartz boat and running according to the procedure described in Sections (D-2) through (D-8). The flux should contain no more than 5 μg of chloride.

2. Weigh 2.0 grams of $\text{Na}_2\text{MoO}_4\text{-MoO}_3$ flux, and place approximately one-half in the bottom of a quartz boat.

3. Weigh out a 0.5 to 1.0 gram sample. Place this on top of the flux, and cover with the remaining flux.

4. Proceed as directed in sections (D-2) through (D-8).

5. After determining the μg chloride, the flux blank should be subtracted before calculating ppm chloride.

F. CALCULATION

$$\text{Chloride (ppm)} = \frac{A}{B}$$

where

A μg chloride.

B sample weight.

G. REFERENCES

1. Rodden, C. J., "Analytical Chemistry of the Manhattan Project", p. 729, McGraw-Hill, New York (1950).

II - DETERMINATION OF FLUORIDE IN TUNGSTEN AND MOLYBDENUM

(Procedure AC-F-1B)

A. METHOD

1. Scope

This method is recommended for the determination of fluoride in tungsten and molybdenum. It is also applicable to such metals as niobium and vanadium and to UO_2 and W- UO_2 composites.

2. Summary

The sample is fused and the fluoride hydrolyzed at 850°C in a stream of moist oxygen. The volatilized HF is absorbed in 50 ml of water, cooled, and treated with an excess of thorium nitrate and hydrochloric acid. "Thoron" reagent is added to form a lake which is bleached by the fluoride. The intensity of the lake is measured photometrically at 545 m μ .

3. Concentration Range

The optimum range is from 10 to 50 μg of fluoride. It may, however, be extended to 90 μg , but consequently suffers a definite decrease in sensitivity.

B. APPARATUS

1. Burrell Electric Furnace, Model H-2.9
2. Beckman Model B Spectrophotometer with matched 5-centimeter cells
3. Quartz reaction tube
4. Quartz boats (3 by 5/8 by 3/8 in.)
5. Steam generator with immersion heater (Aminco Co.) number 1880
6. Erlenmeyer flasks, 250 ml.

C. REAGENTS

Unless otherwise noted, all chemicals are reagent grade. Water is deionized, Grade A.

1. Hydrochloric acid (8.6 percent). Add 86 ml of concentrated hydrochloric acid to 914 ml of water.

2. Thorium nitrate (about 200 μg Th/ml). Dissolve 0.500 gram $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in water and dilute to 1 liter.

3. Thoron reagent (0.05 percent). Dissolve 0.125 gram of O-(2 hydroxy - 3, 6 disulfo 1-1 naphthylazo) benzenearsonic acid, disodium salt in a 250-ml volumetric flask

and dilute to the mark with water. Store in a brown bottle. This solution is stable for only about 2 weeks.

4. Sodium fluoride (10 $\mu\text{g F/ml}$). Place about 0.05 gram of sodium fluoride in a platinum crucible and heat at 600°C for 30 minutes, cool and weigh out 0.0221 gram. Transfer to a 1-liter flask and dilute to the mark with distilled water. This solution should be stable indefinitely if it is then stored in a polyethylene bottle.

5. Sodium Tungstate - Tungsten Trioxide Flux

- (a) Wash thoroughly all the apparatus with water.
- (b) Transfer 165 grams of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ to a 500-ml platinum dish, and heat gently to dehydrate most of the $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$.
- (c) Transfer to a mortar, and add 116 grams of WO_3 .
- (d) Mix with a spatula, and then grind with a pestle.
- (e) Transfer to a 500-ml platinum dish, and heat gently in a hood for about 10 minutes. Then increase the temperature until the bottom of the dish is dull red. Maintain this temperature for about 2 hours.
- (f) Let the melt cool until the top has solidified. Then place the dish on one of two clean dry porcelain trays, and carefully spray a small stream of water on the outside of the dish until the melt has solidified completely.
- (g) Invert the dish on the other tray and tap to dislodge the cake.
- (h) Break the cake into small pieces, then transfer to a mortar and grind into a coarse powder.
- (i) Transfer to a clean, dry, and air-tight storage bottle.

D. CALIBRATION

- 1. Transfer 1.0 ml of $\text{Th}(\text{NO}_3)_4$ solution to each of seven 100-ml volumetric flasks containing approximately 70 ml of water.
- 2. Add 5.0 ml of HCl (8.6 percent) and 1.0 ml of Thoron. (After each addition, rinse the walls of the flasks, and swirl to ensure thorough mixing of reagents).
- 3. Add 0, 10, 30, 50, 70, 90, and 100 μg of fluoride, respectively, to the seven volumetric flasks. Dilute to volume and mix thoroughly.
- 4. Allow the solutions to stand at least 2 minutes before reading the optical density at $545\text{ m}\mu$, using 5-centimeter cells (sensitivity number 2).
- 5. All readings are made using a reference solution containing equivalent amounts of HCl and Thoron.

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E. PROCEDURE

1. Note: Before conducting any analyses, the following daily precautions should be taken:

(a) A reference blank of HCl plus Thoron versus $\text{Th}(\text{NO}_3)_4$, HCl plus Thoron should be made. (This should correspond to ± 0.01 optical density of the zero point on the curve.)

(b) A complete "system blank" should be made. This should correspond to ± 0.01 optical density of the zero point on the curve.

(c) Pipette 50 μg of F into a 100-ml volumetric flask. Add the reagents in the order given in (D-(1)) and (D-(2)) and determine the fluoride from the standard curve. It should read 47.5 to 52.5 (± 5 percent) before samples can be run.

2. Weigh approximately 2 grams of the $\text{NaWO}_4\text{-WO}_3$ flux and place approximately half of it in the bottom of a vitreosil boat.

3. Grind coated particles sample in any small mixer mill using WC or steel grinding balls (grinding time: steel balls, 3 to 4 min; WC balls, $1\frac{1}{2}$ min). Weigh out 0.5 to 1.0 gram sample. Place the sample on top of the flux, and cover with the remaining flux.

4. Adjust the oxygen flow to 3 liters per minute and the steam generator to just at the boiling point.

5. Place the collecting vessel containing 50 ml of H_2O so that the top of the delivery tube is below the surface of the water.

6. Insert the vitreosil boat into the quartz pyrolysis tube which is maintained at 850°C .

7. Pass the oxygen stream over the sample for 15 minutes.

8. Cool the distillate, and transfer it to a 100-ml volumetric flask.

9. Develop and read the complex as described in Section D.

10. After the sample is removed, dump the excess material and allow the boat to cool. Place in a concentrated ammonia solution to clean.

F. CALCULATION

The fluoride content of the sample is determined from the calibration curve.

$$\text{Fluoride (ppm)} = \frac{\text{fluoride found } (\mu\text{g})}{\text{sample weight (g)}}$$

G. REFERENCES

1. Lamont and Conroy, Spectrophotometric Determination of Microgram Quantities of Chloride and Fluoride in Metal Oxides and their Salts, Paper, Pittsburgh Conference, March 5, 1958.
2. Rodden, C. J., Analytical Chemistry of the Manhattan Project, p. 729, McGraw-Hill, New York, 1950.
3. Thomason, P. F., Perry, M. A., and Byerly, W. M., Analytical Chem., 21, 1239-41 (1949).
4. Hillebrand, W. F., Lundell, G. E. F., Hoffman, J. E., and Bright, H. A., Applied Inorganic Analysis, Second Ed., p. 742, (1953).
5. Warf, J. C., Cline, W. D., Tevebaugh, R. D., Analytical Chem., 26, 342-46, (1954).

III - COLORIMETRIC DETERMINATION OF NITROGEN IN MOLYBDENUM AND TUNGSTEN

(Procedure AC-N -1a)

A. METHOD

1. Scope

This method is designed specifically for determination of nitrogen in molybdenum, tungsten, and W-UO₂ composites.

2. Summary

The sample is dissolved in hydrofluosilicic acid and hydrogen peroxide. Phosphoric acid is added, and the solution is heated to remove all traces of peroxide. The resulting solution is made basic with sodium hydroxide, and the nitrogen is separated as ammonia by steam distillation. Ammonia is determined colorimetrically in the distillate with Nessler reagent at 425 m μ . The method is satisfactory for the determination of nitrogen in the range from 10 to 200 ppm.

B. APPARATUS

1. Distilling flasks (100 ml)
2. Distillation apparatus - Scientific Glass Apparatus Catalogue number JM-4190
3. Steam generator with immersion heater, equipped with a powerstat - American Instrument Co., Catalogue number 4-1880
4. Volumetric flasks (50 ml)
5. Spectronic 20 spectrophotometer with 1-centimeter cells.

C. REAGENTS

1. Hydrofluosilicic acid (30 percent)
2. Hydrogen peroxide (30 percent)
3. Phosphoric acid (1 to 1)
4. Sodium Hydroxide (37.5 percent) - 5 pounds in 3750 ml of H_2O
5. Nessler Reagent - Dissolve 50 grams of KI in a minimum volume of cold water (about 35 ml). Add a saturated solution of $HgCl_2$ slowly, until the first slight precipitate of red mercuric iodide persists and then 400 ml of a clarified 9 normal solution of alkali, potassium or sodium hydroxide. Dilute the solution to 1 liter with ammonia-free water and allow to clarify. Remove the clean supernatant liquid for use. The reagent does not deteriorate and can be stored indefinitely.
6. Standard Ammonia Solution ($10 \mu g N/ml$) - Dissolve 3.819 grams of NH_4Cl in water and dilute to 1 liter. Dilute 10 ml of this stock solution to 1 liter.

Prepare all solutions in ammonia-free atmosphere and store in tightly stoppered pyrex bottles. Boil all rubber stoppers used for 30 minutes in sodium hydroxide solution (10 percent), and then rinse in ammonia-free water.

D. PROCEDURE

1. Calibration Curve

Pipette 0 (blank)-, 2-, 4-, 6-, 8-, and 10-ml aliquots (0, 20, 40, 60, 80, and 100 $\mu g N$) of NH_4Cl standard into 50-ml volumetric flasks. Add water to make the volume about 45 ml. Add 1.0 ml of Nessler reagent to each. Dilute to the mark. Stopper and mix thoroughly. Read the absorbance in the photometer using water as a reference. Correct for the blank and plot absorbance against micrograms nitrogen in 50 ml of solution.

2. Sample Analysis

Etch 0.5 to 1.0-gram samples in H_2SiF_6 and H_2O_2 by heating. Rinse with water and let dry. Weigh and transfer to 100 ml beakers. Add 20 ml of H_2SiF_6 and 3 ml of H_2O_2 (30 percent) and heat. If the samples are difficult to dissolve, more of each reagent should be added. After solution is complete, add 15 ml of H_3PO_4 (1 to 1) and heat to remove all traces of hydrogen peroxide. While the samples are dissolving, fill the steam generator flask with water and thoroughly clean the distillation apparatus by passing steam through the entire unit. Collect 50 ml portions of the distillate and add 1.0 ml of Nessler reagent to each. When the absorbance of these solutions indicates that the apparatus is free of ammonia, analysis of samples may proceed. Rinse the sample solutions into 100-ml flasks. Add 25 ml of NaOH solution cautiously to the sample solution so as to form two layers in the flask. Immediately connect the flask to the distillation apparatus. Collect 30 to 35 ml of distillate. Remove the distillation flask and volumetric flask, and add 1.0 ml of Nessler reagent to the volumetric flask. Dilute to

the mark, shake well, and measure the absorbance. (Use 425 m μ when operating the Spectronic 20 spectrophotometer). Carry a reagent blank through the procedure using the same amount of reagents as used with the samples. When the absorbance of the blanks is less than 0.02, zero the blank against water thereby removing the necessity of correcting the absorbance of sample for a blank. The amount of nitrogen is read from the standard curve.

E. CALCULATION

$$\text{Nitrogen (ppm)} = \frac{A}{B}$$

A nitrogen

B sample weight

F. REFERENCE

1. Rodgers and Harter, Anal. Chem. 26, 395 (1954)

IV - DETERMINATION OF URANIUM IN HIGH-PURITY URANIUM OXIDES

(Procedure AC-U-1A)

A. METHOD

Scope

The method exactly as written applied to UO_2 , UO_3 , U_3O_8 , and mixtures of UO_2 - ZrO_2 . The method is applicable to W- UO_2 compositions by using the filtrate obtained in the step C.3 of method AC-W-2A (p. 105).

With modifications of the initial sample treatment procedure to get the sample in sulfate form, it applies to UF_4 , ThO_2 - UO_2 , BeO - UO_2 , UC, U-Zr, and other fuel materials which exhibit no interference with the zinc-dichromate Redox system.

B. APPARATUS

1. Burettes, 100-ml capacity, MCA, precision bore, Scientific Glass Apparatus Corporation
2. Burette 10-ml capacity, micro, with reservoir, precision bore, Scientific Glass Apparatus Corporation
3. Erlenmeyer flasks, quartz, 150 ml, General Electric Company
4. Jones Reductor - funnel type Jones reductor with 30- by 1.9-centimeter reducing column and Teflon stopcock

5. Suction flask, 500-ml capacity

6. Volumetric flask (10-liter capacity), Class A, Scientific Glass Apparatus Corporation

C. REAGENTS

1. 5,6-Dimethyl-1, 10-phenanthroline, G. Frederick Smith Chemical Company

2. Dimethyl Ferroin Indicator (0.025M)

Weigh 1.5600 grams of 5,6-dimethyl-1, 10-phenanthroline into a 150-ml beaker. Add 75 ml of water. Slowly stir in 30 drops of H_2SO_4 (10 percent). Most of the dye will be in solution at this point. Wash into the suspension 0.695 gram $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Continue stirring until all is in solution (about 10 min). Then neutralize to pH 5.0 with NaOH (1M). Dilute the solution to 100-ml volume

3. Ferric chloride (4 percent)

Dissolve 40 grams $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1 liter of water which contains 10 ml H_2SO_4

4. Ferrous ammonium sulfate (0.025N)

Weigh 20.24 grams $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and dissolve in 200 ml of H_2SO_4 (20 percent). When solution is complete, dilute to 2 liters with water.

5. Hydrochloric acid

6. Hydrofluoric acid

7. Mercuric chloride

8. Nitric acid

9. Perchloric acid

10. Potassium dichromate (0.0270N)

Dissolve 13.2390 grams NBS136. Dilute to exactly 10 liters at 25° C.

11. Potassium permanganate (2 percent)

Dissolve 2 grams KMnO_4 in water and dilute to 100 ml

12. Potassium pyrosulfate, powder

13. Sulfuric acid

(5 percent) Cautiously mix 50 ml into 950 ml of water

(10 percent) Cautiously mix 100 ml into 900 ml of water

(1 to 1) Cautiously mix 500 ml into 500 ml of water

14. Uranium Oxide Standard - NBS950

15. Zinc (20 mesh)

16. Zinc amalgam (1.2 percent)

Weigh 250 grams of zinc, 20 mesh, into a 600-ml beaker. Add 300 ml H_2SO_4 (5 percent) and stir until the zinc attains a bright luster (2 to 3 min). Decant the acid solution and rinse the zinc several times with water. Dissolve 4.05 grams HgCl_2 in 400 ml of water which contains 4 ml of HCl . Add the zinc to the mercuric chloride solution. Stir well for 3 to 5 minutes. Decant the acid solution and wash the amalgam several times with water and transfer the amalgam slowly into the Jones Reductor. (Never drop the amalgam into a dry reductor. The reductor should be filled with water when the amalgam is added). Wash the fresh reductor with 300 ml H_2SO_4 (5 percent). Leave the amalgam covered with H_2SO_4 (2 percent) when not in use.

D. PROCEDURE

1. Weigh a uranium sample, about 300 mg, and place into a dry 150-ml quartz Erlenmeyer flask. Add 15 grams of $\text{K}_2\text{S}_2\text{O}_7$, and fuse over an open flame until all the sample is dissolved. Remove from heat and let cool to room temperature.

2. Add 40 ml of water, washing down the sides of the flask, and 3 ml of H_2SO_4 . Place sample on a hot plate and heat until the fused pyrosulfate is dissolved, then bring to almost boiling and add drop-wise KMnO_4 (2 percent) until the pink color in the solution is permanent. Remove from hot plate and let cool.

3. Transfer the sample to a freshly activated Jones Reductor. Allow the sample to flow through the reductor at a rate of 15 ml per minute. Rinse the flask with three-30 ml portions of H_2SO_4 (5 percent), allowing each wash solution to drain to the top level of the amalgam. Finally, wash with three-30 ml portions of water. Remove the suction flask containing the sample from the Jones Reductor and aerate the solution for 15 minutes.

4. Add 10 ml of FeCl_3 (4 percent), 20 ml of H_2SO_4 , 5 ml of HCl (1 to 1), and 1 drop of dimethyl ferroin indicator. Titrate with standard potassium dichromate solution, adding 0.3 to 0.6 ml in excess. Back-titrate with ferrous ammonium sulfate to the reappearance of the orange color.

E. $\text{Cr(VI)}/\text{Fe(II)}$ RATIO

To determine the $\text{K}_2\text{Cr}_2\text{O}_7/\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ ratio, add to a flask 90 ml of water and 90 ml of H_2SO_4 (5 percent), 8 ml of 0.0270 N potassium dichromate solution, 10 ml of FeCl_3 (4 percent), 5 ml of HCl (1 to 1), and 1 drop of dimethyl ferroin indicator. Titrate with 0.025N ferrous ammonium sulfate solution to the appearance of the orange color. The ratio is equal to 8.00 divided by the milliliters of ferrous ammonium sulfate.

F. LABORATORY CONTROL

1. Prior to sample determination each day, two uranium oxide standard samples (NBS950) are carried through the titration procedure. The two standards must check within ± 0.12 percent of theoretical and ± 0.10 percent of each other. If they do not, reagents are checked and pairs repeated until the precision requirement is met.

2. The uranium oxide is treated as follows:

(a) Carefully weigh 0.250 to 0.300 gram of NBS950 standard into a dry 150-ml quartz Erlenmeyer flask. Add 15 grams of $K_2S_2O_7$ and fuse over an open flame until all the sample is in solution. Remove from heat and let cool to room temperature.

(b) Add 40 ml of water, washing down the sides of the flask, add 6 ml of H_2SO_4 (1 to 1). Place the sample on a hot plate and heat until all the flux is in solution. Bring almost to a boil and add drop-wise $KMnO_4$ (2 percent) until the solution is permanently pink. Cool to room temperature and proceed as in section D-4.

3. Each day, on a random basis, a synthetic sample containing a known amount of uranium is carried through the entire procedure. If it is out of control limits, all data obtained up to that point for the day are rerun following any corrective measures that may be required. The reduction-titration system should show a blank of 1 drop of $K_2Cr_2O_7$ or less. Temperature corrections are made on all titrations for room-temperature deviations from $25^{\circ}C$ according to the temperature correction chart.

G. CALCULATIONS

$$\text{Uranium (percent)} = \frac{(B-A) \times 0.0270 \times 117.607 (D) \times 100}{W}$$

where

A $(K_2Cr_2O_7/Fe \text{ ratio}) \times (\text{ml back titration}) + (\text{temperature correction in ml})$;

B ml $K_2Cr_2O_7$ titration;

D equivalent weight of 93-percent enriched uranium. The equivalent weight is calculated for other enrichments according to references 2 and 3;

W weight of sample.

H. REFERENCES

1. Jones, Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle, AEC, 1963.
2. McCluen and Anderson, Gravimetric Factors for Uranium in Selected Compounds, K-1476, June, 1961.
3. New Brunswick Laboratory Volumetric Methods for Uranium Analysis.

- CONFIDENTIAL**
4. Smith and Brandt, 5,6-Dimethyl-1,10-Phenanthroline - Spectrographic Constants as Ferrous Complex and Use as Redox Indicator for Determination of Iron by Oxidation with Dichromate, Anal. Chem. 21, No. 12, p. 948, 1949.

**V - DETERMINATION OF COATING CONTINUITY
BY TRACE URANIUM ANALYSIS
(Procedure AC-U-3B)
(Colorimetric)**

A. METHOD

1. Scope

The method is applied to the determination of the continuity of protective coatings over uranium and uranium oxide fuel materials. Breaks in nitric acid resistant surfaces such as alumina, niobium, niobium-vanadium alloy, tungsten, tantalum, titanium, and pyrolytic carbon are detected by this procedure.

2. Summary of Method

The sample material is warmed in concentrated nitric acid. The nitric acid solution is extracted with tri-n-octyl phosphine oxide. Color is developed in the organic layer by the addition of dibenzoyl methane.

B. APPARATUS

1. Beckman Model B Spectrophotometer with 25 mm cells
2. Separatory funnels, 60 ml, with Teflon stopcocks
3. Teflon beakers, 50 ml

C. REAGENTS

Unless otherwise noted, all chemicals are reagent grade. Water is deionized, Grade A.

1. Acetone
2. Aluminum nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
3. Aluminum nitrate, nitric acid

Dissolve 50 grams of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in approximately 300 HNO_3 . Dilute to 2 liters with water.

4. Cyclohexane
5. Dibenzoyl methane (DBM), 1,3-diphenyl, 1,3-propanedione - EK-2197

6. DBM reagent, 0.5 percent

Weigh 10 grams of 1,3-diphenyl, 1,3-propanedione into a 1-liter beaker and dissolve with methyl alcohol. Add 250 ml of pyridine and dilute to 2 liters with methyl alcohol.

7. Methyl alcohol

8. Nitric acid

9. Pyridine

10. TOPO - tri-n-octyl Phosphine Oxide - EK-7440

11. TOPO reagent - 2 percent

Weigh 20 grams of tri-n-octyl phosphine oxide into a 600-ml beaker and dissolve with cyclohexane. Dilute to 1 liter with cyclohexane.

12. Standard uranium solution - 10 μg uranium/ml

Dissolve 0.2358 gram of U_3O_8 in 20 ml of HNO_3 . Heat to boiling to expel NO_2 fumes. Cool to room temperature and rinse into a 1-liter flask. Add 175 ml of HNO_3 and dilute to volume with water. This solution contains 200 μg uranium/ml.

Mix the 200 μg uranium/ml stock solution well. Pipette 50 ml into a 1-liter flask. Add 170 ml of HNO_3 and dilute to volume with water. Mix the solution thoroughly.

D. PROCEDURE

1. Weigh a 0.5-gram sample into covered 100-ml beaker. Cover with 50 ml HNO_3 . Rapidly heat to 95°C in the covered beaker. Hold at 95°C for 1 hour. Cool and decant the HNO_3 to a second 100-ml beaker. Rinse the sample with water and add this to the sample.

2. Evaporate to about 5 ml volume. Transfer the sample to a 10-ml volumetric flask and dilute to volume. Mix thoroughly.

3. Transfer a 5-ml aliquot to a separatory funnel which contains 10 ml of nitric acid - aluminum nitrate solution. Swirl to mix.

4. Pipette 5 ml of TOPO reagent solution into mixture, stopper, and shake for 2 minutes.

5. Allow phases to separate, drain, and discard the bottom aqueous layer.

6. Wash the organic layer by extraction with 10 ml of nitric acid-aluminum nitrate solution. Discard the aluminum nitrate layer. (Be sure the two layers are thoroughly separated. Carefully drain off a small amount of upper layer by quickly turning stopcock once or twice).

7. Pipette 3 ml of the remaining organic layer into a 25-ml volumetric flask. Dilute to volume with DBM-pyridine mixture. Mix thoroughly.

8. Determine absorbance in 2.5-centimeter cells at $\lambda = 416$ with DBM-pyridine in the reference cell. Determine uranium concentration by reference to a calibration curve.

9. Calibration curve: Pipette aliquots of the uranium standard (10 $\mu\text{g}/\text{ml}$) to contain 0, 20, 40, 100, 200, 250 μg of uranium into separatory funnels containing nitric acid - aluminum nitrate solution. Proceed with the extraction and reading as described from D-3.

E. CALCULATIONS

$$\text{Uranium percent} = \frac{A \times 2 \times 100}{B}$$

where

A μg uranium from calibration curve

B weight of sample.

F. REFERENCES

1. Horton and White, Anal. Chem., 30, p. 1779 (Nov. 1958).
2. White and Ross, Separations by Solvent Extraction with Tri-N-Octyl Phosphine Oxide, NAS-NS-3102 (1961).

VI - GRAVIMETRIC DETERMINATION OF TUNGSTEN IN TUNGSTEN-URANIUM OXIDE COMPOSITES (Procedure AC-W-2A)

A. METHOD

1. Scope

The method is applied to the determination of tungsten in W-UO₂ compositions.

2. Summary of Method

The sample material is oxidized in air. Uranium is separated from the tungsten by nitric acid dissolution. Tungsten is calculated from the weight of WO₃ obtained.

B. REAGENTS

Unless otherwise noted, all chemicals are reagent grade. Water is deionized, grade A.

1. Nitric acid

2. Potassium pyrosulfate, powder

3. Tartaric acid solution (50 percent) - Dissolve 250 grams of tartaric acid in 250 ml of water. Filter into a reagent storage bottle.

C. PROCEDURE

1. Weigh a 0.5-gram sample into a 25-cc platinum crucible. Heat overnight at 775° C to oxidize the metal.

2. Transfer the oxidized sample to a 150-ml beaker. Cover the sample with 25 ml HNO₃, then heat at 90° to 95° C for 3 hours.

3. Cool to room temperature. Dilute the acid with water then filter through a 11-centimeter Whatman number 42 paper. Wash the filter with water. Collect the filtrate and washings in a 500 ml beaker for uranium assay.

4. Add 10 ml of H₂SO₄ (1 to 1) to the filtrate and evaporate to fumes of SO₃. Rinse the Speedivap cover and the beaker walls. Repeat the fuming twice. Proceed with the volumetric uranium assay from (D-2) of procedure AC-U-1A (section IV).

5. Place the wet filter and its contents in a tared 25-cc platinum crucible, carefully heat to remove moisture, then ignite at 775° C. Cool the crucible in a dessicator, then weigh.

6. Cover the residue in the crucible with 5 grams of K₂S₂O₇, and fuse this to a clear melt over a Meker burner.

7. Place the coated crucible and contents in a 250-cc beaker. Cover with 75 ml of tartaric acid solution (50 percent). Warm the mixture until a clear solution is obtained.

8. Rinse the contents of the beaker into a 200-ml flask, and dilute to volume. Mix the solution thoroughly.

9. Transfer a 20-ml aliquot of the solution to a 60-ml separatory funnel for the determination of the uranium which remained with the tungsten. Proceed with the colorimetric uranium determination from (D-3) of procedure AC-U-3B (section V).

D. CALCULATIONS

$$\text{Tungsten (percent)} = \frac{A - B}{C} (0.7930)$$

where

$$A \quad \text{weight of impure WO}_3 \text{ from C. 5}$$
$$B \quad (\text{weight uranium from C. 9}) \times \frac{U_3O_8}{3U}$$

C sample weight

[REDACTED]

E. REFERENCE

1. Hillebrand, Lundell, Hoffman, and Bright, Applied Inorganic Analysis, 1953.

VII - DETERMINATION OF CERIUM IN U-Ce AND W-U-Ce MATERIALS (Tentative method)

A. METHOD

1. Scope

This procedure is for the determination of cerium in $\text{UO}_2\text{-CeO}_2$ and $\text{W-UO}_2\text{-CeO}_2$.

2. SUMMARY OF METHOD

Tungsten-coated samples are first oxidized to permit leaching of the uranium and cerium. Uncoated samples require no treatment prior to dissolution. The samples are dissolved in nitric acid, filtered, and then fumed with sulfuric acid to remove the nitrate. Silver nitrate and potassium persulfate are added to oxidize the uranium and cerium to their highest valence states. An excess of ferrous ion is added to reduce the cerium present. The excess ferrous ion is back titrated with standard ceric solution. A solvent extraction is performed on the WO_3 residue after filtering to determine residual uranium and, from the uranium-cerium ratio, the residual cerium.

B. APPARATUS

1. Beakers - 600 ml
2. Buret - S.G.A.

C. REAGENTS

Unless otherwise noted, all chemicals are reagent grade. Water is deionized, grade A.

1. Ammonium hexanitratocerate IV - (0.1N) Dissolve 109.652 grams of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ in 112 ml of concentrated H_2SO_4 and slowly dilute with vigorous stirring to 2 liters. Standardize the solution with ferrous ammonium sulfate which was just previously standardized with a standard dichromate solution.

2. Ferroin Indicator - $\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3\text{SO}_4$ - 0.025 M - Prepare a 0.001M solution by diluting a 10-ml aliquot of a 0.025M solution to 250 ml.

3. Ferrous ammonium sulfate - (0.10N) - Dissolve 39.5 grams of ferrous ammonium sulfate-7-hydrate in 10 ml concentrated H_2SO_4 and water and dilute to 1 liter. Let stand for 24 hours. Standardize against a standard 0.027N dichromate solution. Determine the $\text{Ce}^{+4}/\text{Fe}^{+2}$ ratio and the titer each day.

4. Nitric acid (specific gravity 1.42)

5. Potassium persulfate

6. Silver nitrate

7. Sulfuric acid (specific gravity 1.84).

D. PROCEDURE

1. Weigh 1.0000 gram of tungsten-coated sample and place in a platinum crucible. (Substrate sample size is 0.5000 g and does not require any treatment prior to dissolving.)

2. Transfer the crucible to a furnace maintained at 400°C for 2 hours. Increase the temperature to 725°C for a minimum of 12 hours or overnight.

3. Rinse the sample into a 600-ml beaker with a minimum of water. Add 75 ml of concentrated nitric acid and heat. When the volume decreases to approximately 25 ml add another 50 ml of HNO_3 . Repeat this procedure twice. (Add nitric acid to the platinum crucible, heat to dissolve any material which may not have been rinsed out, and transfer to the sample in the beaker).

4. After the last HNO_3 addition and heating, cool, and dilute the sample at least 3 to 1 with water.

5. Filter the sample through Whatman number 42 filter paper. Save the residue in the filter paper for solvent extraction determination of residual uranium (see section V).

6. Add 10 ml of concentrated H_2SO_4 to the filtrate and fume. Cool, rinse, and fume again.

7. Bring the volume of the solution to 250 ml

8. Add 0.05 gram of AgNO_3 and 2.00 grams of $\text{K}_2\text{S}_2\text{O}_8$

9. Boil vigorously for 20 minutes

10. Cool, add a 4- to 8-ml excess of ferrous solution and 0.5 ml of ferroin indicator.

11. Back titrate the excess ferrous ion with a standard ceric solution.

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E. CALCULATION

$$\frac{[A - (B) (C)] \times D}{\text{Sample weight}} + E = \text{percent Ce}$$

where

- A ml of ferrous ion added
- B ml of ceric solution required for titration
- C ratio of $\text{Ce}^{+4}/\text{Fe}^{+2}$
- D titer of ferrous solution
- E mg of cerium calculated to be in WO_3

F. REFERENCE

1. C. V. Banks & J. W. O'Laughlin, Anal. Chem., 28, p. 1338 (1956).

VIII - DETERMINATION OF RARE EARTHS IN URANIUM - RARE EARTH COMPOUNDS (Procedure AC-RE-1A)

A. METHOD

1. Scope

Thorium, yttrium, scandium, and all the lanthanons excluding cerium can be determined in the presence of uranium or its oxides over any concentration range applicable to the gravimetric analysis. The rare earth oxides may be examined spectrographically or by X-ray fluorescence for trace uranium contamination.

2. Summary of method

The rare earth - uranium compound is dissolved in nitric acid and the solution is evaporated to dryness. Hydrochloric acid converts the uranium to its anionic chloride complex which is subsequently adsorbed on an anion exchange resin. The rare earth is eluted from the resin and then precipitated with ammonium hydroxide. Any uranium which is precipitated is corrected by X-ray fluorescence analysis.

B. APPARATUS

1. Chromatographic column, plain with Teflon stopcock, 30 mm inside diameter, 250 mm length, 100 ml reservoir

- [REDACTED]
2. 250-, 400-, and 600-ml pyrex beakers
 3. 600-ml vacuum extraction flask
 4. Platinum crucibles, 25 cc

C. REAGENTS

Unless otherwise noted all chemicals are reagent grade. Water is deionized, grade A.

1. Ammonium hydroxide
2. Anion exchange resin AG 1-X8 (Bio Rad Laboratories, Richmond, Calif.) 200 to 400 mesh. This resin is supplied in the chloride form. Excessive fines should be removed from the resin by slurrying with water, then decanting off the fines after a few minutes settling
3. Hydrochloric acid (specific gravity, 1.19)
 - (a) 10 N HCl mix 416 ml of HCl into 84 ml of water in a 600 ml-beaker.
 - (b) 8 N HCl mix 333 ml of HCl into 167 ml of water in a 600-ml beaker.
 - (c) 7 N HCl mix 291 ml of HCl into 209 ml of water in a 600-ml beaker.
 - (d) 0.1 N HCl mix 4 ml of HCl into 496 ml of water in a 600-ml beaker.
4. Methyl red indicator 0.1 percent
5. Nitric acid (specific gravity 1.42)

D. PROCEDURE

1. Dissolution and sample preparation

- (a) Weigh an appropriate amount of sample to yield at least 70 mg or more of rare earth oxide. Transfer the sample to a 250-ml pyrex beaker.
- (b) Dissolve with 50 ml of 1 to 1 nitric acid. Evaporate with heat to dryness.
- (c) Rinse the walls of the beaker with water. Add 10 ml of HCl and evaporate to dryness. Repeat the addition of HCl and evaporation 3 times to convert the uranium to its anionic chloride complex.

(d) Rinse the beaker walls with 10 N HCl. Heat gently to dissolve the salts present. The sample solution is now prepared for transfer to the ion-exchange column.

2. Anion exchange

- (a) Prepare the ion exchange column by mixing 25 grams of Bio Rad AG -1-X8 (chloride form) in water, allowing it to settle, and decanting off excessive fines. Place a small wad of fine glass wool above the exit stopcock plug to support the resin bed. Load the column wet, packing it with a loose fitting plunger as the resin slurry is
- [REDACTED]

poured in; so the resin bed will be firmly and uniformly distributed to prevent channeling and leakage of ions.

(b) The column must now be conditioned to the acidity of the sample. Pass 50 ml of 10 N HCl through the column under vacuum into a 600-ml vacuum flask. Discard the effluent.

(c) Rinse the sample solution into the column reservoir with repeated washings of 10 N HCl. Pass the solution through the column under vacuum into the vacuum flask, maintaining a flow rate of 3 ml per minute, retaining the effluent containing the rare earth. Wash the column with 50 ml of 10 N HCl in 10-ml increments allowing the top of the column to drain dry each time. Try to avoid excessive disturbance of the resin at the top of the column.

(d) The anionic chloride complex of uranium is seen as a bright yellow band at the top of the resin column. A 5 N HCl solution starts to move the uranium band down the column. The resin will quantitatively adsorb the uranium complex at HCl normalities of 6 and greater; successive elutions of HCl in this acid concentration range will effect the separation of uranium and rare earths by retaining the uranium and collecting the rare earth in the effluent.

(e) Pass 75 ml of 8 N HCl in 25-ml increments through the column allowing the top of the column to drain dry prior to the next addition. Avoid disturbance to the resin bed on additions of the 25-ml volumes.

(f) Repeat (e) with 75 ml of 7 N HCl.

(g) After the last 25-ml addition of 7 N HCl has drained through the column, remove the vacuum flask from the ion exchange column. Rinse the contents of the flask into a 600-ml beaker with multiple washings of water. Cover the beaker, place on a hot plate, and evaporate the contents to dryness.

3. Regeneration of the resin

(a) The anion exchange resin can be used for other samples provided the uranium is eluted from the resin.

(b) Pass 150 ml of 0.1 N HCl in 50-ml increments through the column to elute the uranium.

(c) After the uranium elution, the column is conditioned for another sample by the passage of 50 ml of 10 N HCl through the column.

4. Precipitation of the rare earth

(a) Add 20 ml of 1-to-1 HCl to the dry beaker containing the rare earth. Warm to dissolve salts.

- (b) Transfer the solution with multiple washings to a 400-ml beaker.
- (c) Add a small wad of filter pulp and 3 drops of 0.1-percent methyl red solution.
- (d) Add 1-to-1 NH_4OH to the basic side of methyl red. Add 1 ml excess.
- (e) Let stand overnight for the precipitate to digest.
- (f) Filter through number 40 filter paper.
- (g) Rinse the beaker and the precipitate well with 2-percent ammonium chloride solution.
- (h) Transfer the filter containing the rare earth to an ignited and tared platinum crucible; place the crucible under a heat lamp to evaporate excess moisture.
- (i) Transfer the crucible to a muffle furnace and increase temperature to 600°C to ignite carbon. Ignite at 900°C for 1 hour. Cool in a dessicator and weigh the oxide.

5. Carry a synthetic standard through the procedure. Prepare the standard to approximate the sample material as correctly as possible.

E. CALCULATION

$$\text{Rare earth oxide (percent)} = \frac{A \times 100}{B}$$

where

A weight of oxide

B sample weight in grams

F. RESULTS OF SYNTHETIC STANDARDS

1. Rare earth recoveries of 99.9 percent plus have been consistently obtained on standards. All oxides have been analyzed for trace uranium contamination by X-ray fluorescence. Uranium contamination is less than $50\text{ }\mu\text{g}$ on synthetic standards of 1 gram U_3O_8 +0.1 gram of a rare earth.

2. Elution of the anionic uranium complex with 0.1 N HCl with uranium analysis of eluting fractions shows 99 percent of the uranium present in the first 50-ml fraction. Elution of uranium is complete in the second 50-ml fraction.

G. REFERENCES

- 1. C. J. Rodden, Analysis of Essential Nuclear Reactor materials, N.B.L. USAEC, pp. 959 - 965, 1964.
- 2. K. A. Kraus and F. Nelson, Anion Exchange Studies of the Fission Products, from P/837 (USA) Session No. 9B.1, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

IX - DETERMINATION OF YTTRIUM IN THE TERNARY MIXTURE W-Y-U

A. METHOD

Yttrium is determined by X-ray fluorescence following a preliminary chemical separation. Lanthanum is used as a carrier and internal standard.

B. APPARATUS FOR CHEMICAL SEPARATION

1. 125-ml Vycor flask
2. 250-ml Teflon beaker
3. Teflon filtering system
4. Millipore HA45 filters
5. Polypropylene X-ray cells (Spex Industries)

C. REAGENTS FOR CHEMICAL SEPARATION

1. Lanthanum solution (0.8 mg La/ml). Dissolve 938.2 mg of La_2O_3 (Lindsay number 529, 99.997-percent pure) in a 20-percent sulfuric acid solution. Dilute to 1 liter and store in a polyethylene bottle.
2. Yttrium solution (0.2 mg/ml). Dissolve 254.0 mg Y_2O_3 (Lindsay number 1118, 99.999-percent pure) in HNO_3 . Dilute to 1 liter and store in polyethylene bottle.
3. Tartartic acid (5 percent). Dissolve 50 grams of tartartic acid in 1 liter of water.
4. Stock reagents, $\text{K}_2\text{S}_2\text{O}_7$, HF, HNO_3 , H_2SO_4 .

D. PROCEDURE FOR CHEMICAL SEPARATION

1. Weigh 0.100 gram of sample and 3.00 grams of $\text{K}_2\text{S}_2\text{O}_7$ into a Vycor flask. Dry on hot plate for approximately 5 minutes. Cover with a watch glass, and fuse to a clear melt. Cool slowly.
2. Dissolve melt with 35 ml of 5-percent tartaric acid solution using heat as necessary. Transfer to a 250-ml Teflon beaker and dilute to approximately 70 ml with the tartaric solution.
3. Add 5 cc of lanthanum solution (4 mg La) and heat to just below boiling.
4. Add 25 ml of HF and digest for 30 minutes.
5. Filter hot solution through an HA45 millipore filter using Teflon filtering apparatus. Wash incrementally with 1-percent HF.
6. Mount precipitate between sheets of 1/4-mil Mylar stretched across the open end of a polypropylene X-ray cell.

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E. PREPARATION OF STANDARDS

1. Weigh 3.00 grams of $K_2S_2O_7$ into each of 5 Pyrex beakers.
2. Dissolve $K_2S_2O_7$ with 35 cc of tartaric acid solution heating as necessary.
3. Add yttrium solution to beakers as follows: 5, 6, 7, 8, and 9 ml to make standards of 1000, 1200, 1400, 1600, and 1800 μg of Y respectively.
4. Continue with separation procedure as indicated in sections (D-3) to (D-6).

F. EQUIPMENT FOR X-RAY FLUORESCENCE

1. Norelco X-ray spectrograph with bulk sample holder, FA60 W target tube and LiF crystal.
2. Scintillation detector
3. Pulse height analyzer.

G. OPERATING PARAMETERS FOR X-RAY FLUORESCENCE

1. 55 kV and 45 mA
2. Pulse height analyzer settings - 080 base line and 500 window
3. Detector voltage - 815 volts
4. 2θ angles used

YK α - 23.80 $^\circ$

LaK α - 10.59 $^\circ$

Y background - 22.80 $^\circ$

La background - 12.00 $^\circ$

H. MEASUREMENT OF X-RAY INTENSITIES

1. Accumulate counts for standards and samples at the indicated 2θ settings as per the following schedule:

YK α - 256 000 counts

LaK α - 64 000 counts

Y background - 16 000 counts

La background - 16 000 counts

2. Calculate the C/S for peaks and background for standards and samples.

I. CALCULATIONS

1. Determine the Y/LA intensity ratio using the following formula:

$$\frac{Y(C/S) - Y \text{ background } (C/S)}{LA(C/S) - La \text{ background } (C/S)}$$

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2. Plot the Y/La intensity ratio of the standards against the Y concentration in micrograms on linear graph paper. (fig. VII-1).

3. Determine the Y concentration in micrograms in the samples from the curve.
Percent Y in sample = $\mu\text{g Y} \times 10^{-4} / \text{sample weight}$.

J. PRECISION AND ACCURACY

A precision of 2-percent relative at 95-percent confidence is expected with no bias.

K. DISCUSSION

1. Experimental data indicate that $<200 \mu\text{g}$ of tungsten and $<50 \mu\text{g}$ of uranium will be retained on the millipore filter. These concentrations of tungsten and uranium will not affect the Y/La ratio.

2. Good X-ray power supply stability is required to get the indicated precision of 2-percent relative. Because of the proximity of the kV used to the excitation potential of La, a shift of 0.5 kV will affect the La intensity relative to the Y intensity and, in effect, shift the analytical curve.

3. This basic procedure is applicable to any rare earth except cerium.

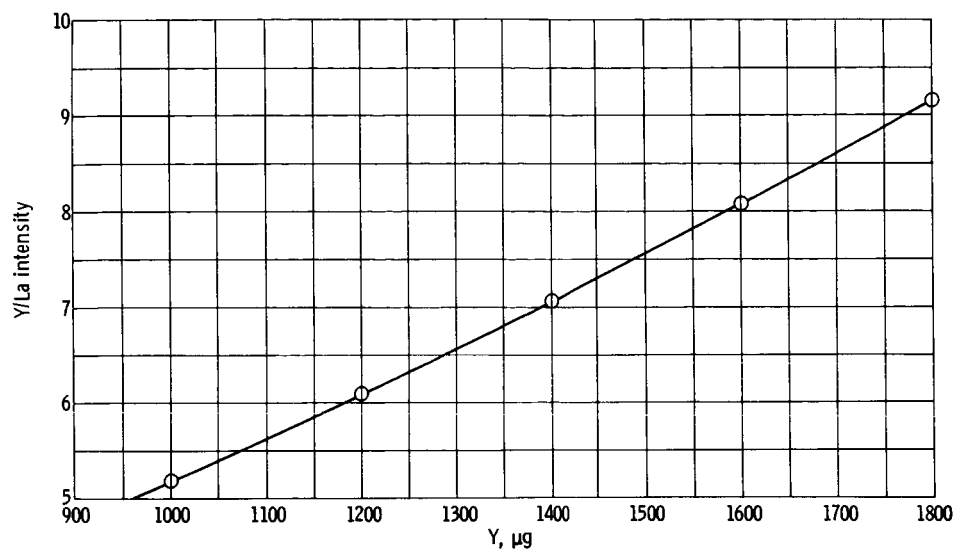


Figure VII. -1. - Yttrium in tungsten-coated $\text{UO}_2 - \text{Y}_2\text{O}_3$.

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VIII. OUTLINE OF ANALYTICAL METHODS USED BY VAL FOR TUNGSTEN - URANIUM DIOXIDE MATERIALS

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SUMMARY

Four methods for determining oxygen-uranium ratios are described. Fluoride is removed by pyrohydrolysis and determined using thorium nitrate. Carbon is determined by a conventional combustion procedure.

INTRODUCTION

The analytical techniques in tungsten - UO_2 systems have been derived from the extensive experience with UO_2 as a fuel for power reactors and the studies on these materials for nuclear thermionic applications.

The authors are indebted to W. Sabol, H. Rosenbaum, F. Wiczorek, and their associates for the development and useful discussions on the techniques described.

ANALYSES APPLIED TO URANIA

There are four techniques utilized for the analysis of oxygen-uranium ratios:

1. X-ray diffraction: shift of lattice spacing as a function of oxygen content. This method is useful for $2.08 \geq \text{O/U} \geq 2.00$.
2. Coulometric titration: determination of U^{+4} and U^{+6} ions. The oxygen-uranium ratio must be in excess of 2.000.
3. Controlled oxidation to U_3O_8 : this method is applicable to hypo- and hyperstoichiometric uranium dioxide.
4. Quantitative metallography: primarily used in hypostoichiometric urania.

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X-RAY DIFFRACTION

This method is a very straightforward one and has been successfully applied at the Vallecitos Atomic Laboratory for over 6 years. The method has been recently extended to $\text{UO}_2\text{-PuO}_2$ fuels. As a result of this experience, the following lattice parameter variation is used

$$a_0 = 5.4707 - 7.404 \times 10^{-2} x$$

for UO_{2+x} ($0.00 < x < 0.08$) at 298°K

Samples of small sizes can be analyzed by this method, and the technique has been verified and cross-checked with the two techniques described below.

Coulometric Titration

The essential feature of this method is the determination of U^{+4} and U^{+6} ions in UO_{2+x} . The method is not applicable to UO_{2-x} . Sample size is generally around 0.5 grams. The sample is granulated under dry deoxygenated conditions prior to dissolution in hot, deoxygenated, phosphoric acid (around 20 cc). The dissolution period is dependent on the oxygen-uranium ratio and particle size and is higher for higher oxygen-uranium ratios. After dilution with 1M H_2SO_4 to about 50 to 60 milliliters, 0.5 milliliter of solution is loaded into a cell. The cell has three electrodes: Pt in H_2SO_4 , Hg (ground), and a reference calomel electrode. In the first step of the analysis, the U^{+6} is reduced to U^{+4} , which determines the amount of U^{+6} present. In the second step, ceric sulphate is added to convert all of U^{+4} to U^{+6} , and the reduction of the total uranium to the U^{+4} state is accomplished. Thus, the total uranium content and the initial U^{+6} content are determined. Four runs are made for each sample. Precision of the determination generally lies between ± 0.0001 and ± 0.001 . The instrumentation is periodically checked by running NBS samples of U_3O_8 and cross-checks with other available techniques.

Oxidation to U_3O_8

This method of oxidizing UO_{2-x} and UO_{2+x} represents the simplest analytical technique and is widely used in the Laboratory. It is the method primarily used for hypo-stoichiometric urania. The oxidation is carried out in one case at 700°C in a 50-50 mix-

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ture of argon in oxygen. The sample size is largely determined by the stoichiometry and weighing balance capability. For 1-gram samples precision of ± 0.006 can be obtained with relative ease. An important factor in oxidation is the grain size of urania. Small grains allow rapid oxidation by grain boundary attack and subsequent sample disintegration. Large grain material can require very long periods of oxidation. It is desirable, but not always necessary, to check the end point oxidation state by coulometric titration.

Quantitative Metallography

This technique has been applied for the determination of the amount of precipitate uranium phase in urania, as a measure of hypostoichiometry of the fuel at elevated temperatures. The main difficulty in the method is sample preparation because pullout or loss of the precipitate phase must be minimized. At present, this technique is being cross-checked with other methods to establish satisfactory procedures.

IMPURITIES IN URANIA

The other impurities in urania are determined by several techniques. Most metallic elements are determined by relatively standard spectrographic techniques which will not be discussed.

Fluorine in Urania

A sample of 10 grams is preferred for this analysis. Pyrohydrolysis at 950°C removes the fluorine which is scrubbed in a NaOH solution. Titration for fluoride ion (thorium nitrate) yields the fluorine level. Experience with this technique has ranged primarily from about 5 to 200 ppm with an uncertainty of ± 20 percent.

A procedure for the microdetermination of fluoride in UO_2 has been established recently (ref. 1). This is a modification of the method developed for fluoride determination in teeth. Urania is dissolved in 10 percent K_2CO_3 - 10 percent H_2O_2 , placed in a Conway diffusion dish, acidified, and incubated at $60^{\circ} \pm 2^{\circ}\text{C}$ for 22 hours. Fluoride is evolved as HF , which is collected in a caustic solution that is contained in a separate compartment of the covered dish. The quantity of fluoride is determined by its bleaching effect on the red zirconium-SPADNS complex. It is necessary to destroy peroxide before diffusion, since it also bleaches the zirconium-SPADNS complex. Interference from aluminum, cesium, thorium, calcium, boron, and silicon in ratios to fluoride of

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1000 to 1 is not observable; however, zirconium interferes seriously at a ratio of 100 to 1.

This method allows the determination of microgram quantities of fluoride in urania. The minimum detectable limit is 0.5 microgram, and sample weights up to 200 milligrams can be used in the procedure. The standard deviation of a single measurement (expressed as percent recovery) varies from ± 16 percent at 1 microgram to ± 1.6 percent at 10 micrograms.

The advantages of this method are (1) the extreme simplicity, (2) the sensitivity, which allows analysis of a very small sample, and (3) the ready adaptability to irradiated fuels, for which no easy method exists.

Carbon Determination

The analysis is accomplished by combustion at 1100°C . The CO_2 produced is absorbed in BaOH and determined by conductivity methods. A 10-gram sample is recommended.

Outgassing

Samples of 10 to 20 grams are heated to 1700°C in vacuum, and the gases are determined by chromatography. Gases encountered are CO , CO_2 , H_2 , O_2 , N , H_2O , NO_2 , etc.

Tungsten in Urania

The basis of this technique has been described previously (ref. 2). The urania is put into solution with nitric-hydrofluoric acid solution. Sulphuric acid is added and taken to fumes. The tungsten is removed as a precipitate by an organic reagent. The precipitate is ignited, and this is followed by carbonate fusion. Molybdenum trace impurities are extracted, and this is followed by a butyl acetate extraction. Spectrophotometry is used to determine the tungsten content. The major experience has been with samples of 16 to 21 ppm, and the precision in that range is ± 2 ppm. The technique can be used down to 1 ppm levels.

ANALYSIS FOR IMPURITIES IN TUNGSTEN

The analyses for interstitials and metallic impurities are accomplished by standard techniques. Problems of fluorine in vapor-deposited tungsten have spurred activity in this analysis. Pyrohydrolysis is used in much the same way as that described for the determination of fluorine in urania.

A considerable effort has been mounted for the determination of uranium in tungsten both before exposure to urania and after a test period.

Samples (0.2 g) are dissolved in a nitric-hydrofluoric acid solution (5 parts 48 per-cent HF, 1 part HNO₃). The volume is adjusted and a spike of U²³³ is added. This fixes 238/233 ratio (or 235/233 ratio). Tributyl-phosphate (30 percent in hexane) is used to separate out the uranium. The separation factor is between 10³ and 10⁴, and the separation is done at least twice. High fluoride content inhibits the separation. The uranium is back extracted into water and the acidity is brought up with 8 molar HNO₃. Dowex 1-by-8 (200-mesh) resin is used to load the uranium, and the impurities such as calcium, fluorine, etc. are eluted with concentrated nitric acid. Elution of uranium is accomplished with 0.5M HNO₃. The sample is then loaded on a filament source for mass spectrometric determination. The ratio of U²³³ to U²³⁸ is determined. The amount of U²³⁸ is obtained as follows:

$$U^{238} = C^{233} \frac{V_{\text{spike}}}{V_{\text{sample}}} \left[\frac{\frac{M_{238}}{233} - \frac{Bl_{238}}{233}}{1 - \frac{\frac{M_{238}}{233}}{\frac{S_{238}}{233}}} \right]$$

where

C concentration of U²³³

M sample + spike

Bl blank

S sample

V volume

The blank used consists of another spike of U²³³. The results show that the pickup of uranium in the analytical steps is an important factor for low levels of uranium in

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tungsten. In fact, it is found to be desirable to assume, a priori, that the sample contains as low as 5 ppm of uranium at the start. The method is capable of analysis of 0.1 to 500 ppm of uranium in tungsten. At 2 ppm and higher, the analysis gives results to ± 5 percent. Below 2 ppm, the uncertainties increase to ± 10 to 50 percent.

REFERENCES

1. Sabol, W. W., and Wills, W. F., Microdetermination of Fluoride in UO_2 , APED-4662, February 15, 1965.
2. Rodden, C. J., (Ed.), Analysis of Essential Nuclear Reactor Materials, AEC Pub. (1964).

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IX. DETERMINATION OF TUNGSTEN AND URANIUM IN TUNGSTEN - URANIUM DIOXIDE CERMETS*

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SUMMARY

A gravimetric method for the determination of tungsten and a spectrophotometric method for the determination of uranium in tungsten - uranium dioxide cermets are described.

INTRODUCTION

Methods originally developed for the analyses of tungsten and uranium in tungsten-uranium alloys have been adapted for the analyses of tungsten - uranium dioxide cermets. The tungsten analysis involves a gravimetric procedure (ref. 1) using α -benzoinoxime and cinchonine as the precipitant in the presence of uranium. A spectrophotometric method (ref. 2) that requires no prior separation of tungsten is used for the determination of uranium.

The procedures used for these analyses are outlined in the following sections.

I. - GRAVIMETRIC DETERMINATION OF TUNGSTEN

Tungsten in tungsten-uranium alloys may be determined using a mixture of α -benzoinoxime and cinchonine as the precipitant (ref. 1). The precipitation is made from a cold sulfuric solution and in the presence of the uranium. The precipitate is ignited at 800⁰ C and weighed as WO₃. Results of 94 determinations on known samples containing 20 to 40 milligrams of tungsten in the presence of 1 to 8 grams of uranium showed an average recovery of 100.1 percent with a standard deviation of 0.7 percent.

* This section unclassified.

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The method was developed for the analysis of tungsten-uranium alloys. It may be applied to the determination of tungsten in W-UO₂ cermet by using as a sample an aliquot of the solution of the cermet. The aliquot should be of such size as to contain between 20 and 40 milligrams of tungsten and should not contain tartaric acid.

APPARATUS AND REAGENTS

Apparatus

Balance, analytical
Beakers, Griffin, Pyrex
Burners, Meker
Cones, filtering, platinum
Crucibles, platinum, 20 milliliters
Filter tablets, ashless, Whatman
Flasks, filtering, 500 milliliters
Furnace, electrical resistance
Paper, Filter, Whatman number 41 H, 9 and 11 centimeter
Trays, 7 by 12 inches

Reagents

α -Benzoinoxime, 2 percent in ethanol, 20 grams of Eastman White Label reagent dissolved in 1 liter of 95 percent ethanol
Cinchonine solution, 100 grams of Eastman White Label reagent dissolved in 1 liter of 18 N Sulfuric acid
Hydrochloric acid, concentrated
Hydrogen peroxide, 30 percent
Ice cubes, made from distilled water
Sodium carbonate, anhydrous, reagent grade
Sulfuric acid, concentrated
Sulfuric acid, 18 N

Wash Solution

Place 8 to 12 ice cubes and 1 liter of water in a 1500-milliliter beaker. Add 5 milliliters of concentrated sulfuric acid, 10 milliliters of the α -benzoinoxime solution, and 5 milliliters of the cinchonine solution. Stir occasionally as the ice melts to keep the whole solution cold and use the solution before all the ice melts.

RECOMMENDED PROCEDURE

Place a weighed sample of the alloy, containing 20 to 40 milligrams of tungsten, in a 400-milliliter beaker. Cover it with water, and add a few milliliters of concentrated hydrochloric acid in small increments. When the vigorous action subsides, add hydrogen peroxide dropwise until the uranium is completely oxidized. If there is an undissolved residue other than tungstic acid in the beaker, filter the solution through Whatman number 41 H paper. Ignite the residue at 800°C , fuse with sodium carbonate, and dissolve the melt in the original filtrate. Add 25 milliliters of 18 N sulfuric acid, $1/4$ of a filter tablet, and 2 ice cubes. Place the beaker in a tray of ice and water and stir until the temperature inside the beaker drops to 0°C . Add, with stirring, 35 milliliters of the α -benzoinoxime solution and 10 milliliters of the cinchonine solution. After 10 minutes, filter with vacuum through Whatman number 41 H paper and wash thoroughly with cold, previously prepared wash solution. Burn off the paper in a tared platinum crucible and ignite the residue at 800°C . Weigh as WO_3 , which contains 79.30 percent tungsten.

RELIABILITY OF METHOD

Standard solutions of uranium and tungsten were prepared from the pure metals. The uranium was dissolved in hydrochloric acid and hydrogen peroxide. The tungsten was dissolved in nitric and hydrofluoric acids, evaporated to dryness with sulfuric acid, fused with sodium carbonate, and the fused mass dissolved in water. From these standards, aliquots were taken to simulate solutions of tungsten-uranium alloys of different tungsten concentrations and different sample size. The tungsten content of these aliquots was determined by the above procedure with the results shown in table IX-I.

TABLE IX-I. - RESULTS OF TUNGSTEN ANALYSES OF KNOWN SOLUTIONS

| Number of deter- minations | Tungsten added, mg | Uranium present, g | Average tungsten found, percent | Standard deviation, percent |
|-------------------------------|--------------------------|--------------------------|------------------------------------|--------------------------------|
| 7 | 40.36 | 1 | 100.2 | 0.7 |
| 12 | 40.36 | 2 | 100.1 | .6 |
| 12 | 20.06 | 1 | 99.6 | .6 |
| 7 | 30.27 | 2 | 99.5 | .5 |
| 12 | 20.09 | 2 | 100.1 | .8 |
| 32 | 30.27 | 3 | 100.4 | .8 |
| 12 | 40.36 | 8 | 100.2 | .6 |
| Total 94 | | | Average 100.1 | Average 0.7 |

CONCLUSIONS

1. Moderate amounts of tungsten in tungsten-uranium alloys can be determined gravimetrically by the use of a combination of cinchonine and α -benzoinoxime as a precipitating reagent.
2. An average recovery of 100.1 percent with a standard deviation of 0.7 percent was obtained for 94 determinations of known amounts of tungsten varying from 20 to 40 milligrams in the presence of 1 to 8 grams of uranium.
3. The method is relatively rapid and simple. No long digestion times are required, and the precipitate does not adhere to the glassware too tightly to be removed with a rubber policeman.

II. - SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

This method was developed for the determination of uranium in alloys of tungsten and uranium when the latter is present in the range between 20 and 65 percent (ref. 2). It has also been applied to the determination of uranium in W-UO₂ cermet. The uranium is determined as the arsenazo complex, without separation from the tungsten, by the method, modified for the purpose, of Fritz and Richard (ref. 3). The arsenazo complex is developed by the addition of arsenazo reagent to aliquots of the sample solution which have been treated with tartaric and boric acids and suitably buffered, and is measured spectrophotometrically at 600 millimicrons. The selectivity of the method is improved by the use of EDTA as a masking agent. Forty-eight determinations of uranium in solutions containing known amounts of uranium and tungsten to simulate alloys containing 20 to

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65 percent uranium gave an average recovery of 99.9 percent with a standard deviation of 0.36 percent for a single measurement. Most of the metallic elements likely to be encountered as impurities can be tolerated in amounts up to 10 percent of the uranium content.

APPARATUS AND REAGENTS

Apparatus

Balance, analytical

Crucibles, platinum, 20 milliliters, with covers

Spectrophotometer, Beckman, Model DU, with 1-centimeter cells.

Reagents

Ammonium hydroxide, 10 percent aqueous solution

Arsenazo, 3-(2-arsenophenylazo)-4, 5-dihydroxy-2, 7-naphthalenedisulfonic acid. Purify the Eastman Organic Chemicals product by slowly dropping a saturated aqueous solution into an equal volume of concentrated hydrochloric acid. Filter off the orange precipitate, wash with acetonitrile and dry at 110° C for 1 to 2 hours. The recovery is about 80 percent. Dissolve 0.500 gram of the product in 1 liter of water.

Boric acid, 1.5 percent aqueous solution

Buffer solution. Dissolve 74.5 grams of triethanolamine and 72 milligrams of disodium versenate in water. Add 14.0 milliliters of nitric acid and dilute to 1 liter with water. This solution is stable indefinitely but should be allowed to age overnight before using.

Hydrofluoric acid, analytical reagent, 48 percent

Nitric acid, analytical reagent, concentrated

Phenolphthalein indicator, 0.25 percent alcoholic solution

Potassium pyrosulfate, analytical reagent

Tartaric acid, 1.5 percent aqueous solution

Uranium standard solution. Carefully weigh about 100 milligrams of Bureau of Standards uranium oxide 950, or the equivalent, dissolve in a little nitric acid, and dilute to 100 milliliters with water.

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RECOMMENDED PROCEDURE

1. Weigh out approximately 100 milligrams of sample, transfer to a 20-milliliter platinum crucible, and add 5 milliliters of nitric acid. Add 6 drops of hydrofluoric acid to the covered crucible, a drop or two at a time, and allow to stand until the reaction ceases. Avoid heating the sample, since that would result in variable losses of hydrofluoric acid.

2. Weigh out 1.5 grams of tartaric acid and place in a clean 100-milliliter volumetric flask. If the sample dissolution with hydrofluoric and nitric acids was complete, transfer the solution to the prepared 100-milliliter flask; be sure the tartaric acid is dissolved, and dilute to the mark with water. (If a residue remains in the crucible, filter the solution into the flask, retaining the residue on number 42 filter paper. Return the paper to the crucible, and burn off the paper over a Meker burner. Add about 1 gram of potassium pyrosulfate and continue heating until a clear melt is obtained. Cool the crucible, extract the melt by warming with a little dilute ammonium hydroxide, and combine with the original solution. Dilute to volume with water.)

3. Transfer an aliquot of the sample solution, of sufficient size to contain 100 to 200 micrograms of uranium, to a 25-milliliter volumetric flask, add 1 milliliter of boric acid solution, and adjust the pH to the phenolphthalein end point with dilute ammonium hydroxide. Add 5 milliliters of buffer solution and 3.0 milliliters (carefully measured) of arsenazo reagent solution. Dilute to volume, mix, and allow to stand for 2 hours. Measure the absorbance at 600 millimicrons using a reagent blank as a reference. To prepare a reagent blank, calculate the amount of tartaric acid contained in the sample aliquot and add a sufficient quantity of 1.5 percent tartaric acid solution to contain this amount to a 25-milliliter volumetric flask. Add all the reagents exactly as for a sample.

4. Prepare a calibration curve by carrying appropriate size aliquots of the standard uranium solution through the procedure.

5. Subtract 0.00028 absorbance unit for each 0.1 microliter of 48 percent hydrofluoric acid calculated to be in the sample aliquot, make any necessary correction for differences in the cells, and determine the uranium content of the sample from the calibration curve.

RELIABILITY

The results of the analysis of known solutions, prepared from a standard uranium and a standard tungsten solution, are shown in table IX-II.

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TABLE IX-II. - RECOVERY OF URANIUM
FROM KNOWN SOLUTIONS

| Uranium present, percent | Tungsten present, percent | Number of determinations | Uranium found, av percent | Standard deviation, percent |
|--------------------------|---------------------------|--------------------------|---------------------------|-----------------------------|
| 20 | 80 | 6 | 100.4 | 0.2 |
| 25 | 75 | 6 | 100.1 | .3 |
| 30 | 70 | 6 | 99.8 | .1 |
| 35 | 65 | 18 | 99.7 | .1 |
| 65 | 35 | 12 | 100.1 | .5 |

Twelve solutions, prepared from separately weighed portions of tungsten metal and containing known amounts of uranium to simulate alloys of 20 to 25 percent uranium, were analyzed in triplicate. The uranium found averaged 99.9 percent, with a standard deviation for a single measurement of 0.40 percent.

REFERENCES

1. Carpenter, R. L.; Gardner, R. D.; Ashley, W. H.; and Henicksman, A. L.: LA-2270 (1959).
2. Hues, A. D.; and Henicksman, A. L.: LA-2844 (1963).
3. Fritz, J. S., and Richard, Marlene J., Anal. Chim. Acta 20, 164 (1959).

DISCUSSION

(Prepared by William A. Gordon)

The discussion portion of the symposium was directed toward clarifying and amplifying the material of the formal presentations and toward defining areas requiring further work. In reporting the ideas developed in this discussion, the editors are departing from the customary question and answer format. Instead, information taken from the tape recordings is summarized here in a style which minimizes the editorial problems arising from the need to assure accuracy of quotations in the statements made by many contributors. Throughout this discussion, therefore, the comments attributed to others are based more on the editors' interpretation of what was said rather than on the actual quotation. When, in the judgement of the editors, a portion of a discussion has significant implications for the analytical problems associated with the analysis of W-UO₂ materials, the contributor is identified by name.

The majority of the discussion was concerned with the significance of the methods relating to fuel stoichiometry. This included discussion of the hydriding method (paper III), the determination of hydrogen-reducible oxides (paper II), and the measurement of weight changes accompanying oxidation and reduction reactions (paper IV). The information developed from using these methods is intended to provide data to the materials researcher that enable him to gain a better understanding of the reactions leading to loss of fuel at high temperatures and ultimate mechanical failure of W-UO₂ fuel elements. They may also aid in elucidating the mechanisms leading to fuel stabilization with the addition of certain metal oxides. Although the interpretation of analytical results is not the primary function of the analytical chemist, a thorough understanding of the basic problem is invaluable, if not essential, in developing analytical techniques which will produce meaningful data. Hence, the discussion of the metallurgical and ceramic details of the W-UO₂ system was included in this symposium.

MEASUREMENT OF FUEL STOICHIOMETRY

In the discussion of the paper presented by F. A. Scott of BNWL (paper II), it was brought out that only one sample, which had been thermally cycled in hydrogen, yielded a significant amount of CO₂ upon reduction with CO. The reducible oxides virtually always were found to require hydrogen for reduction. The water produced by this hydrogen reduction was used by Scott as a measure of the oxygen associated with the tungsten phase. Scott also clarified the question as to why he was able to reduce these oxides in 1½ hours at a relatively low temperature when the fabrication step, involving a hot soak

in hydrogen for 24 hours at high temperatures, apparently did not achieve this reduction of the oxides. He stated that the apparent explanation for this was a matter of a significant oxygen partial pressure in the hydrogen atmosphere used in the fabrication step. After steps were taken to reduce the oxygen partial pressure, the specimens did not show significant amounts of reducible oxides. It was pointed out, however, that W- UO_2 cermet which were thermally cycled in hydrogen evolved hydrogen at 600°C in vacuum, probably because of the presence of free uranium. J. O. Hibbits (GE-NMPO) asked if samples which evolved such gases also showed the presence of reducible oxides. Scott answered that the two conditions, free metal and reducible oxides, have not been found in the same specimen and further stated that he did not believe this to ever be the case.

In the determination of the uranium metal phase in the cermet, J. O. Hibbits and E. A. Schaefer (GE-NMPO) reported that uranium metal located within a UO_2 grain could not be determined because of the low rate of diffusion of hydrogen through the UO_2 grain. In the discussion of this method, it was asked if the use of a higher temperature in the hydriding step would be advantageous to increase the diffusion of hydrogen through the UO_2 grains. Hibbits stated that the as-received specimens described in the paper had been hydrided at temperatures up to 900°C without success. He also stated that they had been unsuccessful in attempts to expose free uranium metal within UO_2 grains by powdering the sample. It was suggested that this problem may be a fruitful area for further research. In answer to a question as to the limit of detection of the hydriding method, it was stated that the smallest amount of uranium metal that could be determined was limited by the hydrogen blank. This blank, in the present system, is about 0.15 cubic centimeters of hydrogen. [Note: an 0.15 cc of hydrogen is equivalent to about 1 mg of uranium metal or about 0.0025 oxygen-uranium atomic ratio units/g UO_2 .]

The discussion turned to the meaning of the term "excess oxygen." It was asked that the term be defined. A. I. Kaznoff (GE-VAL) explained that he believed excess oxygen must be defined by the process or use. Since what is to be avoided in these materials is an interaction between an oxide and a metal, the concept of excess oxygen, in terms of use, is the reactivity of the oxygen. Oxygen, therefore, can only be considered "excess oxygen" if it reacts with the tungsten clad or the tungsten matrix. Since the excess oxygen is defined in terms of reactivity observed in a particular specimen, the only thing one can ask in this type of analysis is the oxygen-metal ratio.

As to possible mechanisms leading to fuel loss and mechanical failure, Kaznoff explained that with UO_{2+x} in the system there is the possibility of forming a W-U-O ternary eutectic. Researchers at Battelle Memorial Institute, Columbus, have reported such a eutectic (ref. 1) and that these eutectics do attack tungsten grain boundaries. However, under the prolonged treatment and reducing conditions at which the tests were run, the eutectic can decompose to form oxygen, UO_2 , and tungsten metal. The evidence for this reaction is the dispersion of tungsten metal in the UO_2 . Kaznoff mentioned tests run at

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GE-Vallecitos under conditions which resulted in total perforation of capsules made of tungsten, molybdenum, or tungsten - 25 rhenium because of this reaction. The other aspect of the problem is the low-temperature decomposition of UO_{2-x} to UO_2 plus uranium metal, which can penetrate the tungsten grain boundaries. During subsequent heat-up cycles, the reverse reaction takes place (i.e., uranium metal recombines with the UO_2 to form UO_{2-x}). This leads to the possibility of a ratcheting mechanism in the grain boundaries involving volumetric changes which, in turn, lead to breakdown of the structure and fuel loss by vaporization. Kaznoff stated that he believes the additive oxides may somehow lower the activity of oxygen so that the oxidation of tungsten is inhibited.

N. T. Saunders (NASA-Lewis) described a postulated explanation for fuel stabilization by addition of M_2O_3 -type oxides. Oxides of this type form oxygen-deficient lattices by vacancy formation. It is generally believed that this type of lattice is more stable and, therefore, prevents the destructive reactions described by Kaznoff. Saunders mentioned that General Atomics, under Lewis sponsorship, is working on a quasi-ternary phase diagram of UO_2 with small additions of M_2O_3 -type oxides to determine if the presence of these oxides causes phase boundary shifts leading to increased solubility of uranium metal (ref. 2). He indicated that preliminary results do not disclose a significant shift in the phase boundary of interest. W. A. Gordon (NASA-Lewis) commented that if the cermet is oxygen deficient through vacancy formation, it would be possible to have a substoichiometric composition in a single-phase system. If this is, in fact, the case, analytical procedures based on the measurement of second phases, such as free uranium or higher metal oxides, would not reveal the substoichiometry. The only alternative analytical methods at present are the determination of total oxygen, discussed later, and the adaption of the oxidation-reduction method presented by S. Kallman and E. W. Hobart (Ledoux). This adaptation, in principle, will provide measurement of oxygen-metal ratios on both sides of stoichiometry. Hobart, however, emphasized that the method does not distinguish between oxygen in the tungsten and UO_2 phases.

In answer to a question as to whether Ledoux has found conditions for oxidizing W- UO_2 materials that avoid undesirable compound formation, Hobart answered that it would be more accurate to say that under the established conditions, the weight gain upon oxidation stops at an equivalent weight of WO_3 and U_3O_8 . This weight gain is not done with a great deal of precision, however, as is the reduction step, which forms well-defined tungsten and UO_2 phases. It was asked why the oxidation reaction was carried so far, that is, why not stop after a definite excess of oxygen has been reached and then continue with the reduction. Hobart answered that, (a) the total oxidation serves to break up solid compacts, and (b) a satisfactory number for total tungsten and total uranium could be derived from the weight gains. These values are sufficiently precise that they subsequently may be used in the calculation of metal in the oxygen-metal ratios. The well-defined end product on reduction is also achieved with mixtures of W- UO_2 . Y_2O_3 ,

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and similar compositions, but it is necessary in these cases to reduce at higher temperatures, that is, about 1100° C.

EFFECTS OF TRACE ELEMENTS ON PROPERTIES

In reply to a question concerning the effects of trace elements on the properties of W-UO₂ cermets, R. M. Caves (NASA-Lewis) summarized the present state of knowledge on such effects as they relate to high-temperature testing of fuel elements. Caves mentioned that in addition to the normal desire to control the quality of materials through the procurement, fabrication, and testing stages, there is a special interest in keeping all extraneous elements to the lowest practicable level because of the unusually high temperatures used in testing. At these high temperatures, virtually all elements picked up will have the effect of lowering the melting point and, therefore, the maximum operating temperature of the fuel element. In addition, at these high temperatures, the impurities may be mobile and react to form second phases, which can weaken the grain boundaries. To minimize the effects of these potential problems, materials used in the Lewis nuclear rocket studies are ordered to a specification of less than 50 ppm (by weight) of any trace metallic elements.

No direct evidence is available on the effects of traces of the metallic elements on the properties or behavior of W-UO₂ composites. However, in the cases of carbon and halogens (chlorine and fluorine), deleterious effects on fuel loss and mechanical properties of W-UO₂ cermets have been observed at impurity levels of 50 ppm carbon and 150 ppm halogens. (Concentrations of halogens up to 3000 ppm may be introduced into cermets formed from tungsten coatings on UO₂ substrate.) In the absence of more definitive data, the Lewis Research Center normally specifies carbon and fluorine at less than 20 ppm each and the total of all halides at less than 75 ppm.

Kaznoff discussed a problem encountered in thermionic work caused by the presence of gas-forming impurities, such as the halogens, in the cermet. Such elements tend to form gas bubbles on the surface of the emitter, which may bridge the interelectrode spacing of 5 to 10 mils. If the impurities are highly segregated, the problem is more severe than if they are uniformly distributed in the fuel material. He suggested, therefore, that in such cases it was of primary interest to determine the degree of segregation of the impurities as well as their average concentrations.

NONDESTRUCTIVE MEASUREMENT OF URANIUM DISTRIBUTION

J. Grey (Martin-Marietta) described a newly developed technique for measuring the uranium distribution in W-UO₂ fuel elements, informally during the discussion period. A

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summary of the method follows.

The technique employs a gamma spectrometer to detect the 185 keV gamma radiation of uranium-235 in enriched W-UO₂ composites. A pinhole mask is placed between the spectrometer crystal and the specimen with the geometry being such that areas between 0.1 and 10 millimeters in diameter are sampled. Variations in uranium concentration as small as 0.1 percent of the amount present can be determined for counting periods ranging from 30 to 120 minutes for each point sampled.

The method is used to monitor fuel elements at a stage of fabrication just prior to sintering and again after completion of sintering. Comparisons of traces made in the two cases reveal changes in uranium distribution occurring during sintering. Grey reported that the migration of UO₂ can be observed when there is a nonuniform temperature distribution or hot spots in the fuel elements during the sintering operations.

DETERMINATION OF TOTAL OXYGEN

In the analysis of W-UO₂ and W-UO₂·M₂O₃ composites, the amount of oxygen can be estimated after determining the concentrations of metal constituents. The direct determination of oxygen in these materials, however, is desirable because a mass balance may then be calculated which affords a more reliable determination of composition. If the direct oxygen determinations are sufficiently precise, they may also be useful in stoichiometric calculations of oxygen-metal ratios. Generally, a precision of 0.2 to 0.5 percent, relative standard deviation, is required for this purpose although precisions better than 1 percent may be useful in some materials research.

The determination of oxygen by the inert-gas fusion method as reported by H. T. Goodspeed (Argonne) was discussed at the symposium. The major point of emphasis was the high degree of success reported by the Argonne group in the accurate and precise determinations of oxygen in W-UO₂ materials. The quantitative accuracy and precision reported for these and other oxide materials are not commonly achieved with commercial inert-gas fusion units. It was of interest, therefore, to compare procedures with regard to instrumentation and experimental technique. In the discussion it was noted that the induction generator supplied commercially for this purpose operates at a frequency of 3 megacycles, whereas the induction generator used in the Argonne work operates at 450 kilocycles. It was suggested that the lower frequency may be more effective in coupling, resulting in a more complete fusion of the specimen and more quantitative reduction of the oxides.

Another feature of the method described by Goodspeed was the use of a crucible cover to prevent mechanical losses of oxide materials from the crucible. Although this innovation has been known for some time, it does not appear to have gained universal

acceptance. It was the consensus of several at the symposium that the use of a crucible cover was highly desirable, if not essential, in achieving precisions of 1 percent or better for oxygen determination in metal oxides.

Some specific experiences were described which appear to substantiate the general observations made regarding the use of kilocycle frequency heating and crucible covers in the inert-gas fusion method. A. Mosen (General Atomics) stated that his laboratory has achieved precisions comparable to those reported by Argonne for oxygen in UO_2 materials. The procedure used was essentially that described by Goodspeed, including the frequency of the induction furnace and the use of a crucible cover. J. Scott and J. Marley (NUMEC) commented that they have used induction furnaces in both frequency ranges and have achieved consistently better results with the lower frequency units. They mentioned, in particular, that the lower frequency generator reduced the tendency to form a corona discharge in the furnace unit and that as a result the blanks tended to be lower than when the higher frequency generator was used. These observations were related only in general terms, however, and it was generally agreed that more definitive information was necessary to determine the relative importance of these and other parameters in oxygen determinations.

DETERMINATION OF HALOGENS

In the determination of halogens by the pyrohydrolysis method, an acidic flux must sometimes be used to promote quantitative decomposition of the halides. The use of such a flux is reportedly also necessary for W- UO_2 materials, particularly solid compacts and tungsten-coated UO_2 particles, in spite of the fact that WO_3 is sometimes used for this purpose in other matrices. Comments made at the symposium indicated an interest in the variations in the use of fluxes in the procedure.

C. W. Weber (ORGDP) reported that V_2O_5 (Fisher Certified Reagent) was used in his laboratory as a flux for W- UO_2 materials, but this flux could be omitted if alkali or alkaline earth halides were known to be absent. Marley and Scott (paper VII) specify the use of Na_2MoO_4 - MoO_3 flux for chloride determinations and NaWO_3 - WO_2 flux for fluorine determinations. Other laboratories are known to employ other variations in experimental procedures including the reagents used in colorimetric measurements.

Lewis Research Center personnel have noted what appears to be systematic variations in the determination of halogens by several different procedures. Therefore, Gordon indicated that a cooperative round robin should be conducted to define analytical problems in this area better.

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REFERENCES

1. Smith, Roy A.; Kizer, Donald E.; Speidel, Edward O.; and Keller, Donald E.: Phase Equilibria in the Uranium-Tungsten-Oxygen System. Rep. BMI-1755, Battelle Memorial Institute, 1966.
2. Langer, S.; Baldwin, N. L.; and Burris, Jr., F. O.: Determination of Effects of Metal Oxide Additions on the Solubility of Uranium in UO_2 . General Atomics Division, General Dynamics. NASA CR-54745, 1965.

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